EFFECT OF ISOTOPE SUBSTITUTION ON THE MAGNITUDE OF NONEQUILIBRIUM NUCLEAR POLARIZATION IN PHOTOLYSIS OF ACETONE IN METHANOL

E. D. Skakovskii, L. Yu. Tychinskaya, S. V. Rykov,
and A. Z. Yankelevich

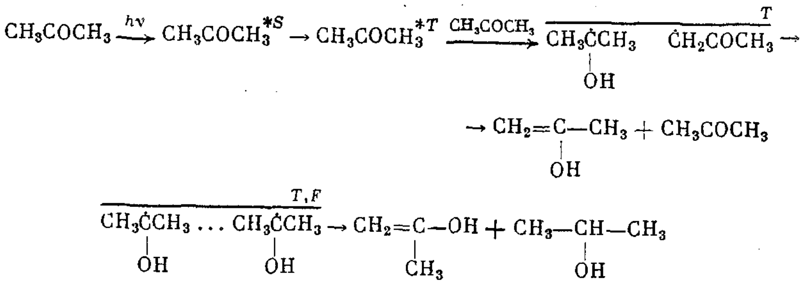
UDC 539.171:541.
141.7:547.284.3

Polarization of nuclei in both the products of the reactions and in the CHD_2OD proton without polarization in the CH_3OH protons is observed in irradiation of a solution of acetone in CD_3OD in the presence of CHD_2OD and CH_3OH. Polarization of the protons of the products is strongly dependent on the temperature of the solution and arises in radical pairs; polarization of the proton of partially deuterated methyl alcohol is due to a mechanism of optical nuclear polarization. It was hypothesized that the isotope effect is due to a difference in proton and electron relaxation and to a difference in the rates of cross-relaxation transitions.

The analysis of the effects of nuclear chemical polarization (NCP) [1] and the appearance of the effects of NCP is usually only explained with the theory of radical pairs [2]. However, in conducting photochemical reactions, the creation of nonequilibrium nuclear polarization whose appearance cannot be interpreted with this theory is possible [3].

The possibilities of creating nonequilibrium nuclear polarization in photolysis of acetone in methanol in conditions where homolysis of acetone takes place inefficiently, i.e., at temperatures <333 K [4], were investigated in the present study.

The PMR spectra of acetone in CD_3OD during irradiation at different temperatures are shown in Fig. 1. No effects of NCP nor products of the reactions were detected below 223 K. At 263 K, acetone and isopropyl alcohol are the basic products. The observed effects of NCP can be explained with the following scheme:



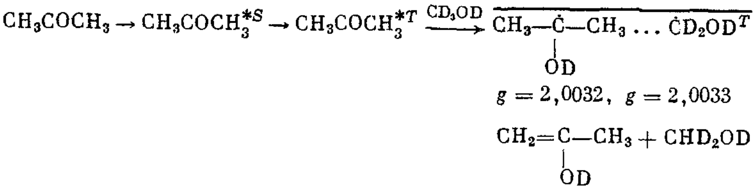
$$CH_3COCH_3 \xrightarrow{h\nu} CH_3COCH_3^{*S} \rightarrow CH_3COCH_3^{*T} \xrightarrow{CH_3COCH_3} \overline{CH_3\underset{\overset{|}{OH}}{\dot{C}}CH_3 \quad \dot{C}H_2COCH_3}^{\,T} \rightarrow$$

$$\rightarrow CH_2{=}\underset{\overset{|}{OH}}{C}{-}CH_3 + CH_3COCH_3$$

$$\overline{CH_3\underset{\overset{|}{OH}}{\dot{C}}CH_3 \ldots CH_3\underset{\overset{|}{OH}}{\dot{C}}CH_3}^{\,T,F} \rightarrow CH_2{=}\underset{\overset{|}{CH_3}}{C}{-}OH + CH_3{-}\underset{\overset{|}{OH}}{CH}{-}CH_3$$

The molecule of triplet-excited acetone cleaves an H atom from a second molecule of acetone with the formation of an acetonyl—hydroxyisopropyl triplet radical pair in which negative NCP occurs on the enol and acetone protons. Multiplet NCP arises in the triplet or uncorrelated pair of hydroxyisopropyl radicals.

In addition to the described effects of NCP, emission of a proton from partially deuterated methyl alcohol, CHD_2OD, present in CD_3OD in the amount of 0.3 M, is observed. In our opinion, the following is the only mechanism by which NCP could have arisen with the participation of radical pairs:



$$CH_3COCH_3 \rightarrow CH_3COCH_3^{*S} \rightarrow CH_3COCH_3^{*T} \xrightarrow{CD_3OD} \overline{CH_3{-}\underset{\overset{|}{OD}}{\dot{C}}{-}CH_3 \ldots \dot{C}D_2OD}^{\,T}$$

$$g = 2{,}0032, \quad g = 2{,}0033$$

$$CH_2{=}\underset{\overset{|}{OD}}{C}{-}CH_3 + CHD_2OD$$

A. V. Topchiev Institute of Petrochemical Synthesis, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 12, pp. 2683-2687, December, 1989. Original article submitted December 2, 1988.

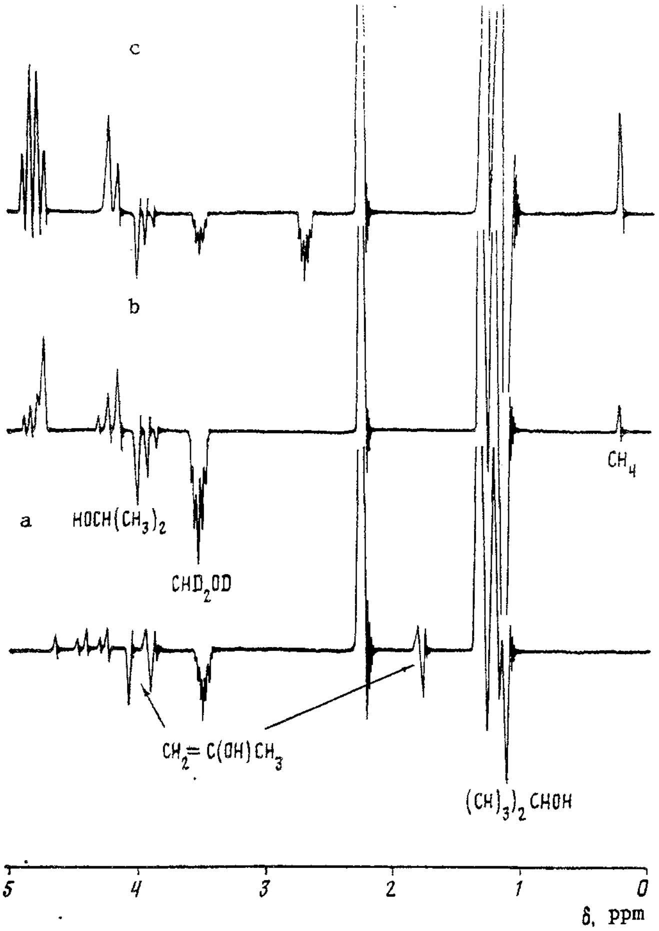


Fig. 1

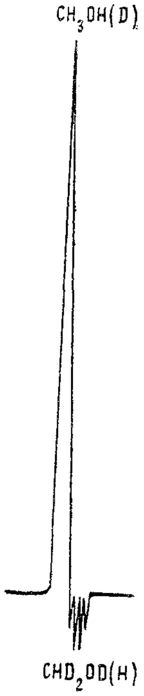


Fig. 2

Fig. 1. PMR spectra of acetone in CD_3OD during photolysis at different temperatures, K; a) 263; b) 333; c) 363.

Fig. 2. Fragment of the PMR spectrum of acetone in CD_3OD in the presence of CH_2D_2OD and CH_3OH during photolysis.

However, in the hydroxyisopropyl—hydroxymethyl radical pair, the difference in the g factors is so small [1, 5] that the creation of marked negative NCP is problematic.

An increase in the temperature to 333 K results in the disappearance of the signals of the enol, which is an unstable compound (Fig. 1b). The intensity of the signals of isopropyl alcohol and the CHD_2OD proton increases. In addition, positive NCP of methane appears, which indicates homolysis of acetone. A further increase in the temperature (Fig. 1c) results in the appearance of the effects of NCP on the protons of the compounds formed from the product of photolysis of acetone, which indicates the high rate of the photochemical reactions. The intensity of the emission signal of the CHD_2OD proton decreases. We also did not find any changes in the concentration of CHD_2OD in the solution (relative error of the measurements: 4%) for almost total photolysis of acetone. The observed effects for the methyl alcohol proton are thus difficult to explain with the theory of radical pairs.

The maximum effect, expressed by the nuclear polarization amplification factor, was:

$$K = \frac{I^* - I_0}{I_0} = -10$$

where I^* is the intensity of the NMR signal during irradiation; I_0 is the intensity of the starting signal.

Irradiation of a 1 M solution of CD_3COCD_3 in CD_3OD in the presence of CHD_2OD (0.3 M) under similar conditions results in the almost total disappearance of the signal of the proton, i.e., K = −1. As a consequence, the nature of the observed effect is identical to the case described above.

It is necessary to note that the intensity of the IR radiation strongly affects K_{CHD_2OD} and virtually does not alter K for the protons of the products of the reactions.

We advance the following hypothesis for explaining the observed effects of negative nuclear polarization of the CHD_2OD proton: nuclear polarization is created by a mechanism of dynamic nuclear polarization (DNP) or optical nuclear polarization (ONP) during cross-relaxation transitions (CRT) in the complex (exciplex) of the triplet-excited acetone molecule with the methanol molecule. It was hypothesized that the triplet electron levels of acetone are populated unevenly. It was natural to verify whether nonequilibrium nuclear polarization is created in exciplexes of acetone with protonated methyl alcohol.

A fragment of the NMR spectrum of photolysis of acetone (1 M) in the presence of CHD_2OD (0.3 M) and CH_3OH (0.3 M) is shown in Fig. 2. Emission of the CHD_2OD proton is observed and the intensity of the signal of CH_3OH virtually does not change. When NCP appears, the polarization amplification factor is proportional [6]

$$K \sim k' T_{1n} E \qquad (1)$$

where k' is the rate constant of formation of exciplexes which participate in the creation of NCP; T_{1n} is the nuclear spin-lattice relaxation time in the observed group of nuclei; E is the polarization coefficient.

For a dipole—dipole mechanism of relaxation, the ratio of the relaxation times of the proton bound in one molecule with D or H atoms can theoretically attain values of $T_D/T_H \sim 16$ [7]. We were unable to experimentally measure precisely the ratio of the relaxation times of the protons of the methyl group of the system in methyl alcohols due to overlapping of the signals. However, the measurements conducted showed that the relaxation times differ significantly.

The rate constant of formation of exciplexes is a function of the intensity of the light, the concentration of the reactants, the viscosity of the solution, the temperature, etc., manifested in the same way both in the case of deuterated and in protonated methanol.

However, the process of electron spin-lattice relaxation, which decreases the magnitude of NCP, competes with the process of formation of NCP as a result of CRT

$$k' = k \cdot p = k \frac{k_{\text{cross}}}{\frac{I}{T_{1e}} + k_{\text{cross}}} \qquad (2)$$

where k is the overall rate constant of formation of exciplexes; p is the fraction of exciplexes participating in the CRT; k_{cross} is the rate constant of CRT; T_{1e} is the electron spin-lattice relaxation time.

CRT usually take place more slowly than spin-lattice relaxation [8] and, for this reason, Eq. (2) can be transformed as follows:

$$k' = k \cdot k_{\text{cross}} \cdot T_{1e} \qquad (3)$$

The efficiency of the cross-relaxation processes is a function of the number of magnetic nuclei in addition to the other conditions [9]. The dependence of the probability W of nuclear CRT in the system AX_n on the number of nuclear spins, known from the literature, is additional confirmation. It follows from [10] that

$$\frac{W^{CH_3}}{W^{CHD_2}} \sim \frac{1}{\sqrt{3}} \sim \frac{1}{1.8} \qquad (4)$$

An isotropic and anisotropic hyperfine interaction can affect the electron spin-lattice relaxation times as a result of molecular motions [11]. For isolated molecules in optimum conditions, $1/T_{1e} \sim n_{\text{nuc}}$, i.e., in our conditions

$$\frac{T_{1e}\,(3\ \text{protons})}{T_{1e}\,(1\ \text{proton})} \sim \frac{1}{3} \qquad (5)$$

In consideration of the above, the polarization amplification factors and consequently also the observed effects in the PMR spectrum of the photolyzed mixture for CHD_2OD and $CH_3OH(D)$ can theoretically differ by more than 80 times. Nonequilibrium nuclear polarization will consequently be marked only on the hydrogen atoms of the CHD_2OD molecules under these conditions.

EXPERIMENTAL

Photolysis was conducted on 1 M solutions of acetone in CD_3OD. Irradiation was conducted directly in the modified detector of a BS-487 NMR spectrometer with a quartz light conductor. A DRSh-1000 mercury lamp was used as the light source. The intensity of the light flux was no less than 10^{17} quanta/sec. The products were analyzed by GLC and NMR spectroscopy.

LITERATURE CITED

1. I. P. Gragerov, L. A. Kiprianova, and A. F. Levit, NCP in Studying the Mechanism of Reactions of Organic Compounds [in Russian], Naukova Dumka, Kiev (1985).
2. A. L. Buchachenko, R. Z. Sagdeev, and K. M. Salikhov, Magnetic and Spin Effects in Chemical Reactions [in Russian], Nauka, Novosibirsk (1978).
3. E. D. Skakovskii, S. V. Rykov, L. Yu. Tychinskaya, and Ya. N. Malkin, Izv. Akad. Nauk SSSR, Ser. Khim., 1890 (1987).
4. S. V. Rykov, G. A. Nikiforov, and E. D. Skakovskii, Izv. Akad. Nauk SSSR, Ser. Khim., 2601 (1987).
5. S. P. Vaish, R. D. McAlpine, and M. Cocivera, J. Am. Chem. Soc., 96, 1683 (1974).
6. A. L. Buchachenko, Chemical Polarization of Electrons and Nuclei [in Russian], Nauka, Moscow (1974).
7. A. Abragam, The Principles of Nuclear Magnetism, Clarendon, Oxford (1961).
8. V. I. Valyaev, Yu. N. Molin, and R. Z. Sagdeev, Preprint, Institute of Chemical Kinetics and Combustion, Siberian Branch, Academy of Sciences of the USSR, Novosibirsk (1987).
9. K. M. Salikhov, Chem. Phys., 64, 371 (1982).
10. V. A. Daragan, T. N. Khazanovich, and A. U. Stepanyants, Chem. Phys. Lett., 26, 89 (1974).
11. A. Carrington and A. D. McLachlan, Introduction to Magnetic Resonance, Harper and Row, New York (1967).