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O. A. Gaidukevich, researcher (IPhOCh, NAS RB);
Ye. D. Skakovsky, PhD (Chemistry), assistant professor (BSTU);
L. Yu. Tychinskaya, PhD (Chemistry), chief researcher (IPhOCh, NAS RB);
T. D. Zveryeva, senior researcher (IPhOCh, NAS RB); **Ye. A. Dicusar**, researcher (IPhOCh NAS RB);
S. A. Lamotkin, PhD (Chemistry), assistant professor (BSTU)

COMPARATIVE ANALYSIS OF DIACYLATED PEROXIDE METHANOL SOLUTION DECOMPOSITION UNDER TEMPERATURE AND MICROWAVE RADIATION

Thermolysis of benzoyl and acetylbenzoyl peroxides in methanol-d_4 under temperature and microwave radiation treatment was studied. It was shown that chemical induced dynamic nuclei polarization can be observed even when reaction is carried out in spectrometers with high magnetic fields. In this case spin correlation in geminate radical pairs with labile aceloxy radicals persists. Equal quantity of products is obtained independent of the way of peroxide decomposition initiation. Homolysis proceeds according to chain mechanism. Contribution of induced decomposition decreases while reaction proceeding. Molecules of dissolved oxygen terminate the chain effectively, decreasing the rate of the reaction of peroxide decomposition. In the case of acetylbenzoyl yield of products depends of initiation mechanism: under microwave radiation treatment molecules of solvent are more active, but dissolved oxygen is less active than under thermolysis condition.

Introduction. Diacylated peroxides (DP) are widely used in polymer production, besides they are indispensable reagents in organic synthesis. Peroxide molecules have different structure and high reactivity, whereupon they are widely used as models in researching different problems of fundamental chemistry.

Thermal decomposition of DP is presented in detail in the monograph [1]. To determine the details of DP decomposition mechanisms solvents which don't undergo chemical reactions were used. However, such solvents as alcohols interfere the decomposition process actively. Besides, they absorb microwave radiation effectively. Peroxide reactions in alcohols as well as the influence of dissolved oxygen on thermal decomposition have been studied insufficiently.

Thermal decomposition of benzoyl peroxide (BP) in methanol-d_4 has been investigated [2]. It has been ascertained that decomposition proceeds according to the chain mechanism, the chemically active oxygen inhibiting thermolysis.

Microwave radiation has been recently used in the chemical practice. We found no publications studying DP decomposition under microwave radiation. It is obvious, that the advantage of the microwave radiation effect on reactive mixtures (in comparison with other types of heating) means decrease of the reaction time [3].

The aim of the research is comparative analysis of DP decomposition in methanol-d_4 under temperature and microwave radiation. To ascertain thermolysis details chemical nuclei polarization (CNP) effects have been analyzed.

Main Part. BP and acetylbenzoyl peroxide (ABP) were chosen as research objects because of their availability and wide use in polymerization reactions. Besides, in the process of homolysis they yield phenyl radicals characterized by enhanced resistance to oxygen and active acetyloxy radicals (in the case with ABP) [4].

Methanol-d_4 – primary alcohol yields the least number of reaction products thus facilitating analysis.

^{1}H NMR spectroscopy was used to analyze reaction products. 0.01 mol BP and ABP solutions in methanol-d_4 have been analyzed. The solutions were sealed in the quartz ampoules-"inserts" (tubes with the outer diameter 4 mm) which were placed in standard NMR ampoules (5 mm) at regular intervals during the reaction time to record the spectra. Some samples were deaerated by repeated freezing with liquid nitrogen and defrosting at decreased pressure. Others were oxygenized, frozen and sealed. Thermolysis was carried out in an oil thermostat at 343 K and in a drier at 498 K. The samples were subjected to the microwave radiation in a microwave "Electronica SP -10" (capacity – 600 W, operating frequency – 2,450 MHz). The spectra were recorded with operating frequency 500 MHz in a "quanti-tative" regime by an AVANCE-500 spectrometer (Germany). Chemical shifts were measured relative to CHD_2OD signals (solvent impurity $\delta = 3.30$ ppm).

To study CNP effects inserts with peroxide solutions were placed into the preliminarily heated spectral sensor (353 K). Deuterium stabilization and magnetic field uniformity regulation were further carried out. Spectra recording (16 accumulations) was carried out after 3 min of the immersion of the sample in the heated sensor. The procedure was repeated several times during decomposition.

The following chemical proton shifts for peroxides were obtained. BP δ, ppm: ortho – 8.07; para – 7.74; meta – 7.59; ABP: ortho– 8.01; para – 7.71; meta – 7.55, CH – 2.25.
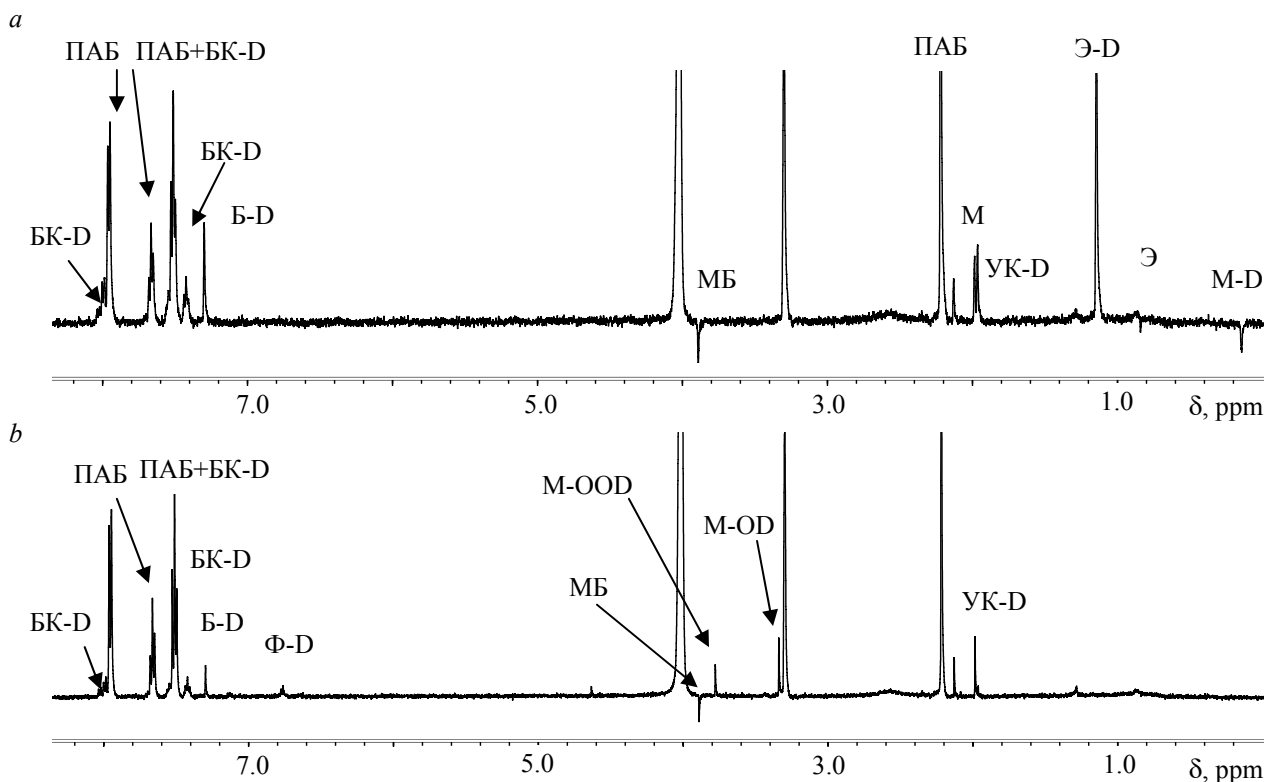
Fig. 1. NMR spectra of ABP in methanol-d recorded at 353 K:
a – deaerated; *b* – oxygenized solution

A number of compounds were obtained during decomposition process and identified δ, ppm: benzoic acid-D ($C_6H_5C(O)OD$, БК-D, ortho – 8.01; para – 7.58; meta – 7.47); benzol-D (C_6H_5D, Б-D, 7.32); phenylbenzoate ($C_6H_5C(O)OC_6H_5$, ФБ, ortho – 8.17; para – 7.69; meta – 7.55; ortho – 7.21; para – 7.29; meta – 7.44); methylbenzoate ($C_6H_5C(O)OCH_3$, МБ, ortho – 7.97; para – 7.55; meta – 7.42; CH – 3.85); phenol-D (C_6H_5OD, Ф-D, ortho – 6.75; para – 6.78; meta – 7.14); methylacetate-D_3 ($CH_3C(O)OCD_3$, МА, CH – 2.02); acetic acid-D ($CH_3C(O)OD$, УК-D, CH – 1.98); methane-D (CH_3D, M-D, 0.18); ethane (CH_3CH_3, Э, 0.84); ethanol-D, $1D_2$ (CH_3CD_2OD, Э-D, 1.15); methanol-D, (CH_3OD, M-OD, 3.39); methyl-D hydroperoxide (CH_3OOD, M-OOD, 377).

Because of the long life of benzoyloxyl radical ($\sim 10^{-8}$ s [5]) we failed to detect CNP effects in the spectral sensor while heating BP solutions. This factor results in the small yield of the "cell" product and the loss of spin correlation in geminal phenylbenzoyloxyl radical pair (RP).

On the contrary, ABP thermolysis (Fig. 1) results in CNP effects. Positively polarized protons are Б-D and Э-D, negatively polarized are methyl protons МБ, Э, M-BD. There is no aromatic protons polarization, except Б-D.

Thus, the "cell" product polarization forms in the singlet benzoyloxy-methyl РП according to the $S-T_0$ mixture mechanism. Therefore, though magnetic field intensity value is rather high (11.7 T), spin correlation in the indicated РП retains. This is characteristic for CNP while working on spectrometers with iron magnets. Э-D, Э, M-D are "yield" products of the geminate РП and methyl group proton polarization in these substances must be positive. However, for Э and M-D products it is negative, which means that in this case methyl proton polarization has higher coefficient of amplification in the uncorrelated methyloxymethyl-d_3 РП. Fig. 1. NMR spectra of ABP in methanol-d_4 recorded at 353 K: a – deaerated; b – oxygenized solutionЭ emission testifies rather a long life of methyl radicals as well as the existence of associates with ABP molecules which support formation of their recombination product. Otherwise, due to the spin-lattice relaxation in methyl radicals the Э CNP would have disappeared quickly.

Thus, under ABP thermolysis due to the short lifetime of acetyloxy radicals (10^{-10}–10^{-9} s [6]) there exists CNP on the proton products even in high magnetic fields.

Fig. 2 shows NMR spectra of the decomposition products of deaerated BP solutions under: *a* – temperature (2 h at 343 K), *b* – microwave radiation (3 min).
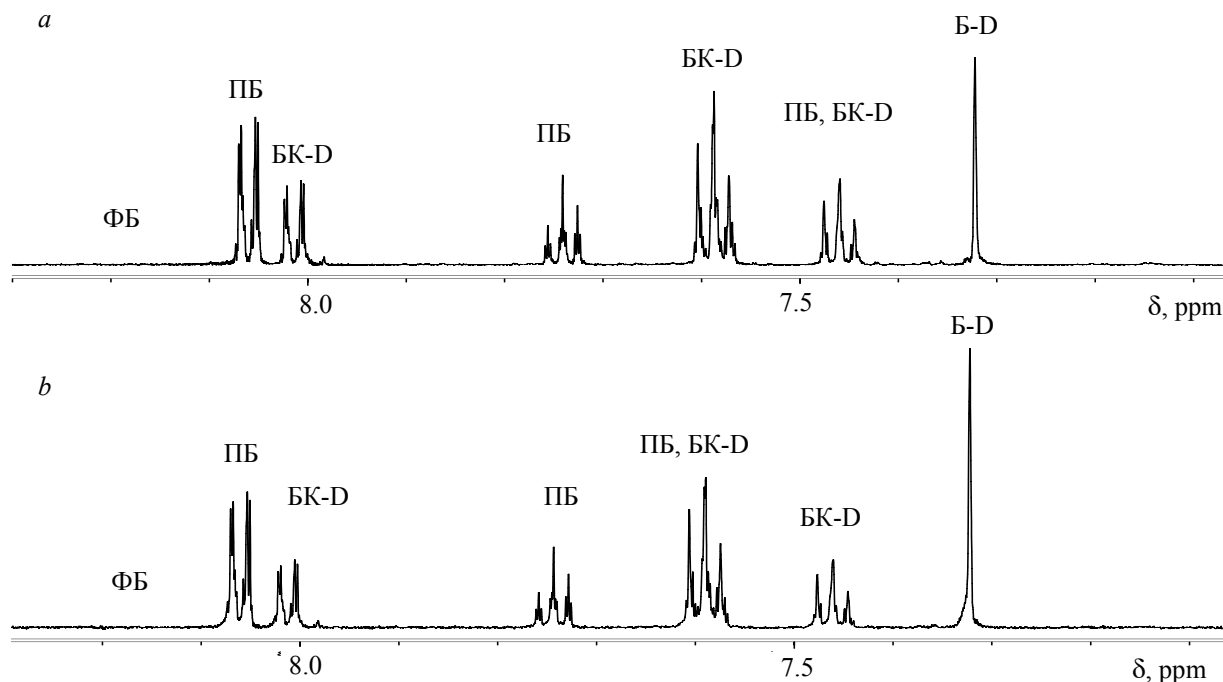
Fig. 2. NMR spectra of the decomposition products of deaerated BP solutions under:
a – temperature (343 K); *b* – microwave radiation

The degree of BP decomposition in both cases is 40%. It is obvious that the spectra practically don't differ from each other. It's possible to obtain the same result if BP samples are saturated with oxygen, though decomposition in this case occurs slower (8% in 2 h). Such dependence is connected with the fact that BP decomposition proceeds with a large number of chain processes which are terminated by dissolved oxygen.

Thus, different methods of peroxide decomposition initiation yield practically the same homolysis products. Peroxide decomposition results in long-lived radicals providing the solvent absorbs and transforms energy from an external source to the peroxide.

Fig. 3 demonstrates NMR spectra of the decomposition products of deaerated ABP solutions under: *a* – temperature (2 h at 343 K); *b* – microwave radiation (2 min). The degree of decomposition in both cases is 60%. The figures demonstrate that in both cases the same products are formed. But their quantitative content in solutions is different. It is especially evident for substances having been formed from acetoxy peroxide fragment. Thus, samples affected by microwave radiation contain a larger amount of МБ, Б-D, МА, Э-D and Э, at the same time the amount of БК-D and УК-D decreases. Besides, the polymer yield increases (δ, ppm): CH_2 – 1.30, CH_3 – 0.88.

Since under microwave radiation the temperature of the sample volume increases additional thermolysis is necessary. The thermolysis was being carried out at 498 K for 5 minutes, the temperature regime being equal to the one under mi-

crowave radiation. The yield of thermolysis products is comparable with that formed under microwave radiation. In this case the yield of MA is much less than that of УК-D. It means a more active involvement of the alcohol molecules in the decomposition process under microwave radiation.

Fig. 4 presents NMR spectra of the decomposition products of the oxygenated ABP solutions under: a – temperature (17 h at 343 K); b – microwave radiation (2 min). The degree of peroxide decomposition is 75%. Comparing Fig. 3 and 4 we may ascertain that oxygen decreases ABP thermolysis notably, while under microwave radiation this influence is much less. Besides, in solutions having been subjected to thermolysis the yield of МБ, БК-D, МА, М-OD, M-OOD and Ф-D is higher than that in the compounds formed under microwave radiation. On the contrary, the yield of Б-D, УК-D, М-D, Э and Э-D is less.

Thus, under ABP thermolysis at 343 K oxygen reacts with radicals resulting in the appropriate products. It also prevents radicals from eliminating the atom of deuterium off the solvent. At the same time (as in the case with BP) oxygen prevents induced ABP decomposition and consequently decreases its rate.

At the same time while enhancing the molecule energy microwave radiation destroys weak complexes of peroxide and oxygen molecules, thus stimulating chain processes. Increase of temperature has the same effect. However, as it was mentioned above, the role of active solvent molecules increases in the course of a reaction under microwave radiation.
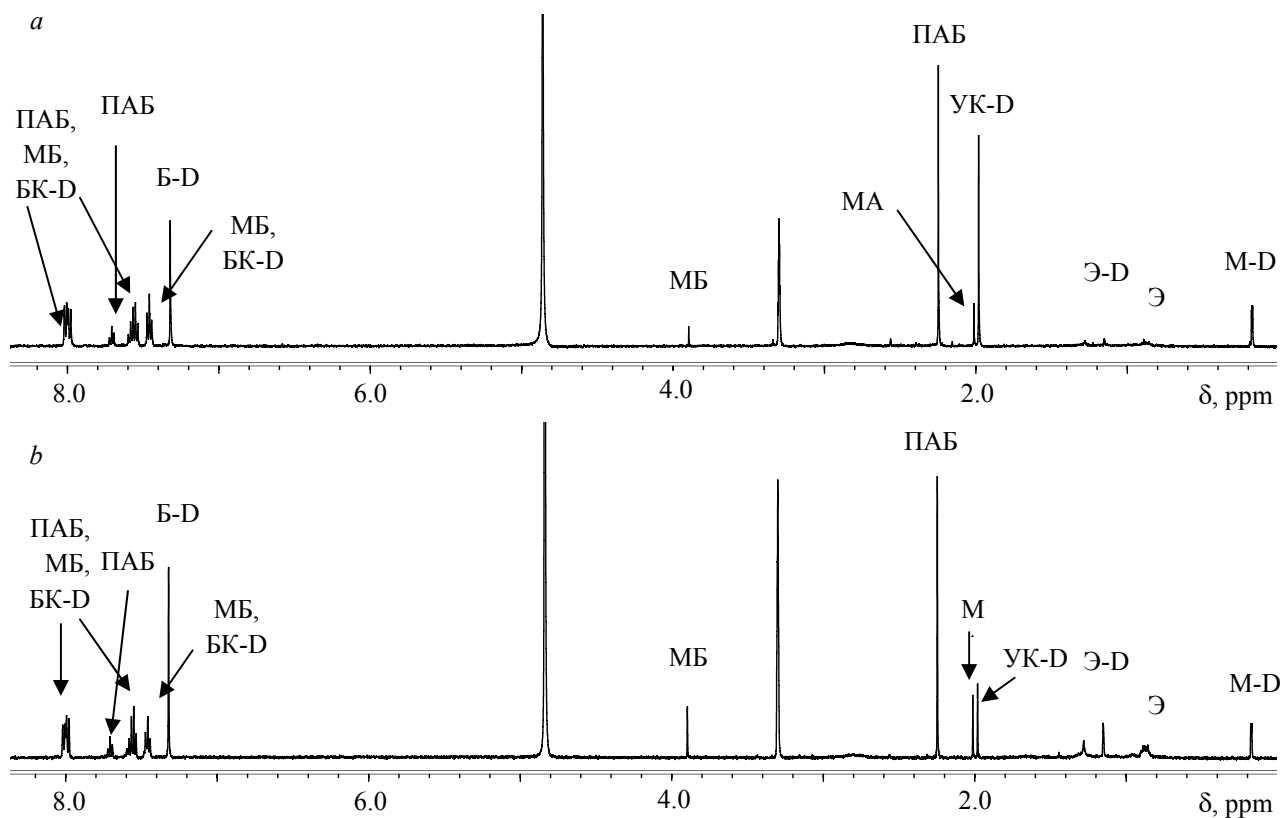
Fig. 3. NMR spectra of decomposition products of deaerated ABP solutions under:
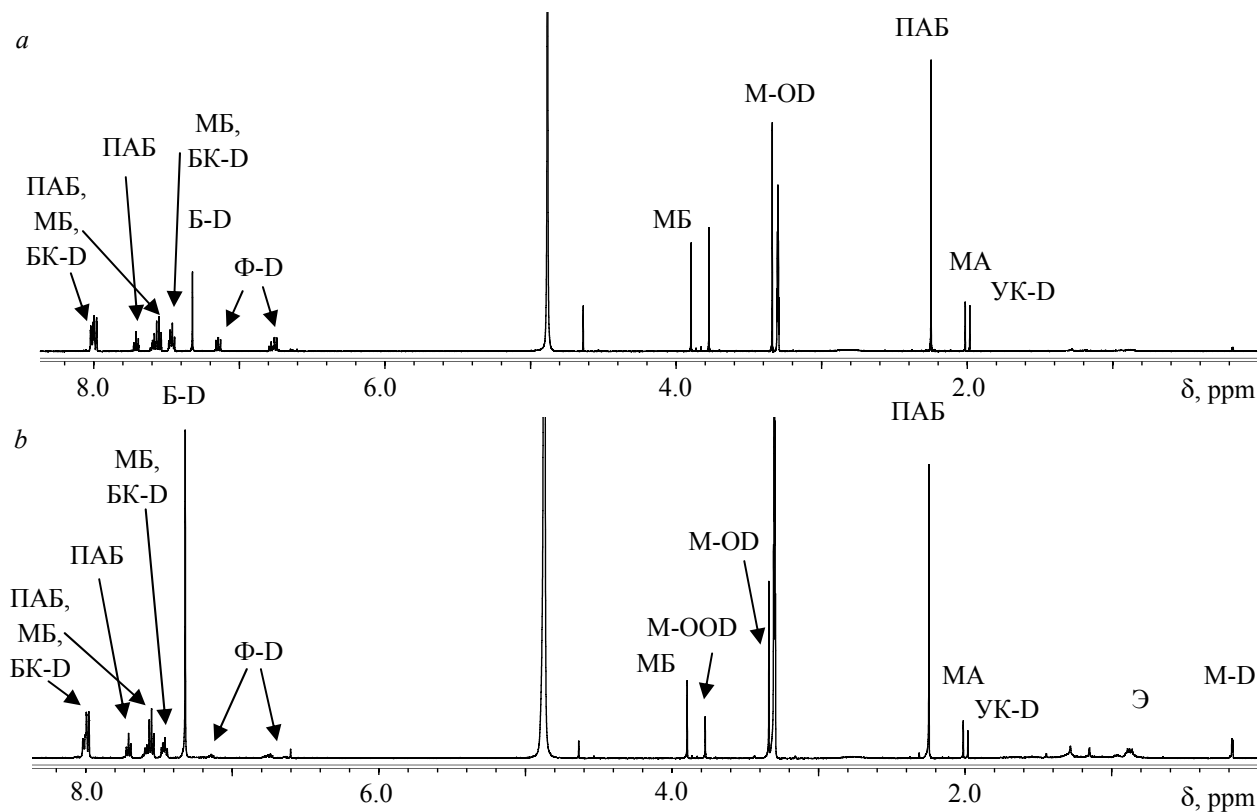*a* – temperature (343 K); *b* – microwave radiation

Fig. 4. NMR spectra of decomposition products of the oxygenized ABP solutions under:
a – temperature (343 K); *b* – microwave radiation

Conclusion. In the result of research it has been ascertained that spin correlation retains in geminate radical pairs in spectrometers with strong magnetic fields. In this case we observe CNP under thermolysis of peroxide solutions which decompose resulting in labile aceloxy radicals. Decomposition of benzoyl peroxides resulting in long-lived benzoyloxy radicals proceeds in the same way as the one under temperature and microwave radiation. Decomposition of acetylbenzoyl peroxide resulting in short-lived acetyloxy radicals proceeds under microwave radiation, the partition/amount of active solvent molecules being higher than that under thermolysis.

References

1. Антоновский, В. Л. Физическая химия органических пероксидов: монография / В. Л. Антоновский, С. Л. Хурсан. – М.: Академкнига, 2003. – 391 с.

2. Влияние кислорода на разложение метанольных растворов пероксида бензоила / О. А. Гайдукевич [и др.] // Труды БГТУ. Сер. IV, Химия и технология орган. в-в. – 2008. – Вып. XVI. – С. 21–25.

3. Бердоносов, С. С. Микроволновое излучение в химической практике / С. С. Бердоносов, О. Г. Бердоносова, И. В. Знаменская // Химическая технология. – 2000. – № 3. – С. 2–8.

4. Russel, G. A. The reactivity of phenyl radicals toward molecular oxygen / G. A. Russel, R. F. Bridger // J. Amer. Chem. Soc. – 1963. – Vol. 85, Issue 23. – P. 37 765–37 766.

5. Den Hollander, I. A. Radical pair substitution in chemically induced dynamic nuclear polarization. Cooperative effect / I. A. Den Hollander // J. Phys. Chem. – 1975. – Vol. 10, Issue 2. – P. 167–184.

6. Скаковский, Е. Д. Время жизни ацилоксирадикалов, образовавшихся при разложении пероксида ацетилпропионила / Е. Д. Скаковский, С. А. Ламоткин, Л. Ю. Тычинская // Журн. прикл. спектр. – 1997. – Т. 64, № 3. – С. 306–311.