way analogous to S_N2 mechanism usually occurring at *sp*^{3} hybridized carbon [11]. However, our recent DFT (density functional theory) calculations [12] failed in prediction of a transient state, instead they predict formation of the tetravalent transient product (Fig.4) that seems stable in vacuum an solvent cage as well. This makes the case slightly more complicated, therefore further clarification of the mechanism requires additional experimental and computational effort.

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References

[1]. Davies M.J.: Photochem. Photobiol. Sci., 3, 17-26 (2003).
[2]. Clennan E.L.: Acc. Chem. Res., 34, 875-884 (2001).
[3]. Jensen F., Greer A., Clennan E.L.: J. Am. Chem. Soc., 120, 4439-4449 (1998).
[4]. Pogocki D., Ghezzo-Schöneich E., Celuch M., Schöneich C.: Singlet oxygen induced oxidation as a benchmark of the conformational flexibility of Met-$(X)_n$-Met peptides. In: Europhysics conference abstracts. Vol. 28A. European Physical Society, 2004, p.77.
[5]. Pogocki D.: Wewnątrzcząsteczkowe przemiany rodnikowe z udziałem utlenionego centrum siarkowego w modelowych związkach tioeterowych o znaczeniu biologicznym. Instytut Chemii i Techniki Jądrowej, Warszawa 2004, 87p. Raporty IChTJ. Seria A No. 2/2004, in Polish.
[6]. Pogocki D.: Acta Neurobiol. Exp., 63, 131-145 (2003).
[7]. Zahn R. *et al*.: Proc. Natl. Acad. Sci. USA, 97, 145-150 (2000).
[8]. Nowakowska N., Kępczyński M., Dąbrowska M.: Macromol. Chem. Phys., 201, 1679-1688 (2001).
[9]. Bobrowski K., Pogocki D., Schöneich C.: J. Phys. Chem., 97, 13677-13684 (1993).
[10]. Bartosz G.: Druga twarz tlenu. Wolne rodniki w przyrodzie. Wydawnictwo Naukowe PWN, Warszawa 2003, pp.1-447, in Polish.
[11]. Smith M.B., March J.: March's advanced organic chemistry reactions, mechanisms, and structure. John Wiley, New York 2001.
[12]. Frisch M.J. *et al*.: Gaussian 03. (Rev. B.03). Gaussian Inc., Pittsburgh, PA 2003.

ELECTRON PARAMAGNETIC RESONANCE STUDY OF ETHYL RADICALS TRAPPED IN SYNTHETIC H-rho ZEOLITE

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Depending on the adsorption pressure, two types of ethyl radicals were observed in γ-irradiated H-rho zeolite exposed to C_2H_4. The first type of ethyl radical has shown hyperfine couplings with α and β protons very similar to those observed for ethyl radicals in liquid hydrocarbons at low temperature. The hyperfine coupling with α-protons (A_α=1.47 mT, A_β=2.7 mT, g_{iso}=2.0029) of second ethyl radical is significantly reduced suggesting a strong interaction of ethyl radical with zeolite through the methylene group.

The primary radiolytic processes of small organic molecules have been one of the most fundamental subjects in radiation chemistry. A number of EPR (electron paramagnetic resonance) and optical absorption studies have been reported for organic radicals stabilized in different halocarbon matrices at low temperature. Also inert gas matrices have been utilized for that purpose very successfully. Synthetic zeolites because of the crystalline lattice structure, variable pore size and ion exchange properties, are unique to study the chemistry of reactive intermediates in heterogeneous systems. The EPR technique and related methods like ENDOR (electron nuclear double resonance) as well as NMR (nuclear magnetic resonance) spectroscopy are among the most appropriate methods for the investigation of molecules or radicals trapped in different zeolites [1,2].

The EPR spectra of ethyl radicals generated in liquid or solid phase or trapped on solid surfaces at low temperature are well known. In liquids, ethyl radicals have been characterized by isotropic hyperfine parameters. In contrast, radicals adsorbed on a surface have an asymmetric line profiles typical for axially symmetric spin Hamiltonian parameters [3,4].

The NaCs-rho zeolite synthesized by the modified Robson's method in cationic form was exchanged three times with 20% solution of NH_4NO_3 followed by calcination at 573 K in air for 20 h to prepare the protonic form of zeolite [5].

The samples of H-rho zeolite were placed into Suprasil EPR tubes and dehydrated *in vacuo*, whilst gradually raising temperature to 473 K. Then oxidation with static O_2 at 573 K was carried out for 2 h. The oxygen was pumped off at the same temperature for the next 2 h. The adsorption of ethylene was carried out at room temperature at a pressure of 0.4 and 8 kPa for 24 h and then the zeolite samples were irradiated in a ^{60}Co source at the liquid nitrogen temperature (77 K) with a dose of 5 kGy. The EPR measurements were carried out with an X-band Bruker ESP-300E spectrometer equipped with a Bruker ER 4111 VT variable temperature unit operating in the temperature range 110-370 K. The g-value was determined using a DPPH specimen for field calibration.

The EPR spectrum of γ-irradiated H-rho/C_2H_4 zeolite exposed to 0.4 kPa of ethylene at room temperature and recorded at 110 K consists of two sets of lines: **A** – relatively intensive multiplet (A_α=2.7 mT, A_β=2.15 mT, g_{iso}=2.0028) of ethyl radicals and triplet **B** – representing $^{\bullet}CH_2$ radicals (A_{iso}=2.0 mT, g_{iso}=2.0027) (Fig.1). The hyperfine coupling constants are independent of temperature and are very similar to hyperfine constants of ethyl radicals in other matrices – in frozen hydrocarbons or at the

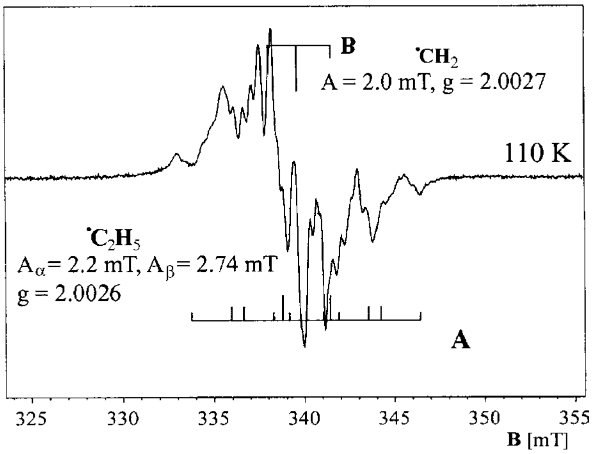

Fig.1. The EPR spectrum of γ-irradiated H-rho zeolite exposed to 0.4 kPa of C_2H_4 recorded at 110 K.

surface of silica gel at low temperature. The EPR spectrum of the ethyl radicals was observed in the temperature range 110 to 250 K. Isotropic hyperfine parameters and high thermal stability suggest that ethyl radicals are trapped in the middle of α-cages and do not interact with surface of zeolite. The observed line broadening of $^•C_2H_5$ lines can originate from hindered rotation of the CH_3 group at lower temperatures. It is worthy of mention that we did not observed the EPR spectrum of vinyl radicals although the radiolysis of liquid ethylene leads to the formation of that radical product.

The EPR spectrum of H-rho zeolite with ethylene adsorbed under a pressure of 8 kPa and recorded at 230 K is shown in Fig.2a. Spectrum of this radical is observed in the temperature range 150-310 K and is completely different from the spectrum of ethyl radicals presented in Fig.1. It consists of two overlapping EPR spectra of two different radicals: **B** – triplet of $^•CH_2$ radical with EPR parameters (A_{iso}=2.0 mT, g_{iso}=2.0027) similar to those in rho zeolite exposed to 0.4 kPa of C_2H_4 and **C** – multiplet with anisotropic spin Hamiltonian parameters (A_α=1.47 mT, A_β=2.7 mT, $g_\perp$=2.0026, $g_{||}$=2.0029) similar to the spectrum of ethyl radicals adsorbed on VYCOR glass surface [6]. That spectrum was assigned to the ethyl radical strongly interacting with the surface of zeolite. The spectrum in Fig.2b presenting the sum of two EPR spectra simulated with the following parameters: **A** – A_{iso}=2.0 mT, g=2.0027 and ΔH_{pp}=0.15 mT; **B** – A_α=1.47 mT, A_β=2.7 mT, $g_\perp$=2.0026, $g_{||}$=2.0029 and ΔH_{pp}=0.75 mT is in good agreement with experimental spectrum.

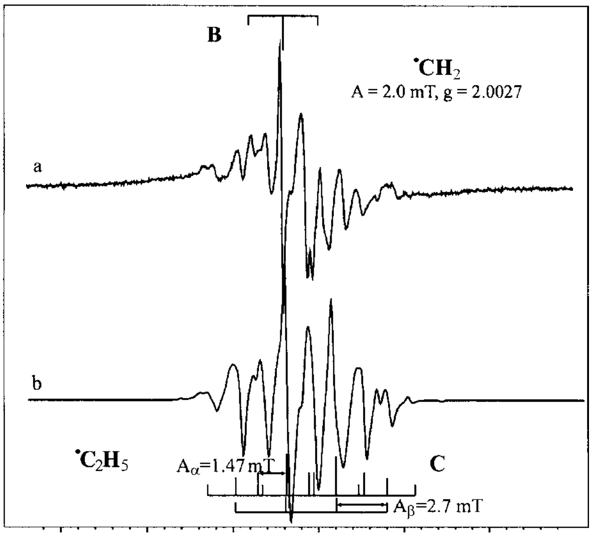

Fig.2. The experimental (a) and simulated (b) EPR spectra of γ-irradiated H-rho zeolite with ethylene adsorbed under a pressure of 8 kPa.

It is interesting that α hyperfine constant of $^•C_2H_5$ (**C**) is distinctly different from α hfc of typical ethyl radical (**A**), while β hfc constants in both types of ethyl radicals are nearly the same. It might be due to the strong interaction of ethyl radical with trapping sites (Brönsted acid sites and/or exchangeable cation sites) through the methylene group. Another possible origin of the large difference in α hyperfine constant of both types of $^•C_2H_5$ radicals might be related to the pressure of adsorbed gas. It is postulated that at higher pressure C_2H_4 molecules migrate to the less accessible sites in zeolite framework. Then methylene groups could be trapped in octagonal windows or prisms while CH_3 groups would stay outside and not participate in the strong interaction with zeolite.

It has been proved that H-rho zeolite shows unique properties for stabilization of small alkyl radicals. Those radicals, usually very reactive, in H-rho lattice are stable even at 310 K. Depending on the adsorption conditions, two different types of ethyl radical were observed. The first type is characterized by isotropic spin Hamiltonian parameters and corresponds to freely tumbling radical stabilized in electrostatic field of zeolite. The second type strongly interacts or even is chemically bonded to the aluminasilica framework. In γ-irradiated zeolite rho containing ethylene, the EPR spectra of ion-radicals were not observed. Thus, it seems reasonable to assume that $^•CH_2$ radicals are formed as a result of fragmentation of ethylene molecules.

References

[1]. Toriyama K., Nunome K., Iwasaki M.: J. Chem. Phys., 77, 5894 (1999).
[2]. Iwasaki M., Toriyama K., Muto H., Nunome K., Fukaya M.: J. Phys. Chem., 85, 1326 (1981).
[3]. Fessenden R.W., Schuler R.H.: J. Chem. Phys., 39, 2447 (1963).
[4]. Shiga T., Lund A.: J. Phys. Chem., 77, 453 (1973).
[5]. Robson H.E., Shoemaker D.P., Ogilvie R.E., Manor P.C.: Adv. Chem. Ser., 121, 106 (1973).
[6]. Katsu T., Yanagita M., Fujita Y.: J. Phys. Chem., 75, 4064 (1971).