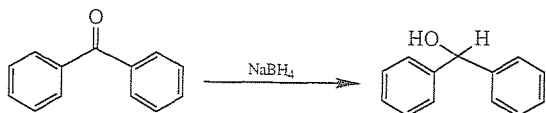


**PS11.04.07 THE REACTIVITY OF SOLID BENZOPHENONES TOWARDS SOLID-STATE REDUCTION: STRUCTURAL AND THERMODYNAMIC ASPECTS.** Dirk Abeln, Stefan Ebbinghaus, Jürgen Kopf and Matthias Eppe, Institute of Inorganic and Applied Chemistry, University of Hamburg, Martin-Luther-King-Platz 6, D-20146 Hamburg, Germany

Benzophenone can be reduced to benzhydrol by simply mixing the solid compound with solid sodium borohydride ( $\text{NaBH}_4$ ) and leaving the mixture at room temperature for a few days [1,2]:



This interesting reaction could be of interest as a "reaction without solvent", that is highly desirable for ecological, economic and toxicological reasons.

We studied the kinetics and the feasibility of this reduction reaction for a number of substituted benzophenones. The crystal structure should play an important role for this kind of solid-state reaction, therefore the structures of a number of benzophenones and benzhydrols were determined by single-crystal X-ray diffractometry. Additionally, experiments with thermal analysis (DSC), scanning electron microscopy and NMR were performed. In some cases this reaction, which was originally postulated as pure solid-state reaction [1], occurs *via* intermediate liquid phases. These could be identified as eutectic mixtures of benzophenone and benzhydrol.

[1] F.Toda, K. Kiyoshige, M. Yagi, *Angew. Chem. Int. Ed. Engl.* **28** (1989) 320-321.

[2] M.Eppe, S. Ebbinghaus, A. Reller, U. Gloistein, H.K. Cammenga, *Thermochim. Acta* **269/270** (1995) 433-441.

**PS11.04.08 EFFECT OF CAESIUM AND STRONTIUM ON REAL STRUCTURE OF FELDSPAR AND CARBONATE MINERALS.** V.V.Akimov and V.L.Tauson, Institute of Geochemistry, Irkutsk, 664033, Russia

The processes of the defects generation under mechanical dispersion of minerals are studied using the crystals of potassium feldspars and calcium carbonates from the genetically different deposits. The type and characteristics of dislocation structure are estimated as a function of dispersion time in the ball-mill planetary activator and mineral sample to milling balls mass ratio. It is shown that different channels of relaxation of structural strains are realized depending on chemical composition of samples: the defects formation and their ordering (polygonization of dislocations), and the redistribution of impurities throughout the crystallite accompanied by the formation of their complexes with the dislocations. The physicochemical modelling of the effect of fractionation of impurities into imperfect crystals by computer (Tauson & Akimov, 1992) showed that caesium stabilizes the regular dislocation structures (dislocation walls and nets) in potassium feldspar whereas strontium stabilizes the dislocation defects in carbonates (calcite and dolomite). This is supported by the data on submicroscopical structure obtained by the Fourier analysis of diffraction line profiles. After a lapse of dispersion time, the size of coherently scattering blocks is stabilized and only microstrains are changing. The change in the starting temperature of Cs vapour generation under thermal atomic absorption analysis in graphite furnace also supported the presence of dislocation-assistant Cs in K-feldspar. The data obtained are important for the creation of effective technology of the burial of wastes containing radioactive isotopes of Cs and Sr by use of imperfect mineral crystals in the synrocks.

This study is supported by MacArthur Foundation.

Reference Tauson V.L. & Akimov V.V. (1992) *Atomic Energy* **72**, p.251-255.

**PS11.04.09 INVESTIGATION OF KINETIC OF DEHYDROXYLATION REACTION IN MUSCOVITE.** M. T. Dehtyruk, E. A. Kalinichenko, A. S. Litovchenko, A. M. Kalinichenko, N. N. Bagmut, Institute of Geochemistry, Mineralogy and Oreformation, Ukrainian Academy of Sciences, Palladina prosp., 34, 252680, Kiev-142, Ukraine

Structural transformation of hydroxyl-containing minerals are usually accompanied by destruction of the structural OH- groups (the dehydroxylation reaction). It is followed by partial or complete rebuilding of the crystalline structure. This effect can be evoked by temperature, electric field, radiation etc. At the temperatures above 900 K the dehydroxylation reaction take place in a muscovite.

The kinetics dependences  $a(t)$  of the dehydroxylation reaction and the temperature dependence  $k(T)$  of the dehydroxylation rate, studied in the muscovite by Electron Spin Resonance method, are presented in this work. Samples of a polycrystalline muscovite (Ukraine) by dimensions 1.0x1.0x0.1 mm had been subjected to the thermal treatment within the temperature range 923 to 1173 K.

The theoretical analysis of experimental data shown that the kinetics curves  $a(t)$  is well described by the exponential law. The temperature dependence  $k(T)$  can be described by the theory of transitions, induced by fluctuative reparation of a barrier as a result of thermal oscillations of ions in the lattice. On the basis of the kinetic and temperature dependences of the dehydroxylation reaction the two-well curve of proton potential energy was calculated taking into account thermal oscillations of ions in the muscovite structure.

**PS11.04.10 INTERMEDIATE STRUCTURE OF CARBON ATOM FROM NONBONDED  $\pi$ - $\pi$  INTERACTION TO  $\sigma$ -COVALENT BOND.** T. Ishida<sup>1)\*</sup>, Y. In<sup>1)</sup>, H. Nagata<sup>1)</sup>, C. Hayashi<sup>1)</sup>, M. Doi<sup>1)</sup> and A. Wakahara<sup>2)</sup> <sup>1)</sup>Department of Physical Chemistry, Osaka University of Pharmaceutical Sciences, 2-10-65 Kawai, Matsubara, Osaka 580, Japan, <sup>2)</sup>Fujisawa Pharmaceutical Co., Ltd., 2-1-6 Kashima, Yodogawa-ku, Osaka 532, Japan

Two kinds of Cu(II) complex crystals (**1** and **2**) of pyridoxal-5-phosphate (PLP)pyridoxamine-5-phosphate (PMP) Schiff base were obtained during the *in vitro* Cu(II)-mediated transamination reaction of L-alanine by PLP.

Concerning the intermolecular carbon...carbon short contact, the distance less than 3.4 Å, which corresponds to the sum of van der Waals radii for aromatic carbon atom, is generally thought to be very unstable because of the strict van der Waals repulsion. However, the X-ray crystal analysis of **1** showed unusual C...C short contacts of ~2.3 Å between the  $\text{=CH=N=CH=}$  fragments of the centrosymmetrically related Schiff bases, which correspond to an intermediate distance of the intermolecular  $\pi$ - $\pi$  short contact and the usual  $\sigma$ -covalent bond. On the other hand, the X-ray crystal analysis of **2** showed the structure in which one of these two C...C short contact pairs observed in **1** was covalently bonded.

Judging from these X-ray results and other spectroscopic data, the crystal structure of **1** could correspond to the first presentation of the carbon  $Sp^2 \rightarrow sp^3$  transition state at the atomic level, and the appearance of its structure is primarily due to the delicate/elaborate combination of (i) the Cu(II)-mediated deprotonation (production of carbanion) of azomethine carbons [ $\text{=CH=N=CH=}$ ] (ii) the structural stability of ligand molecule reinforced by the pyramidal coordination of Cu(II) ion and (iii) the sparing solubility of **1** in the acidic reaction solution, resulting in the inhibition of transition to **2** and the precipitation of **1**. The chemical and structural features of short contact carbon atom in **1** have been discussed by reference to the structure of **2**. The *in vitro* Cu(II)-dependent formation of complexes **1** and **2** from PLP and amino acid have been also considered.