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

Benzenophenone can be reduced to benzhydrol by simply mixing the solid compound with solid sodium borohydride (NaBH₄) 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 benzenophenones. The crystal structure should play an important role for this kind of solid-state reaction, therefore the structures of a number of benzenophenones and benzhydrols were determined by single-crystal X-ray diffractionometry. Additionally, experiments with thermal analysis (DSC), scanning electron microscopy and NMR were performed. In some cases this reaction, which was originally postulated as a solid-state reaction [1], occurs via intermediate liquid phases. These could be identified as eutectic mixtures of benzophenone and benzhydrol.


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, Mineralogy and Oreformation, 664033, Russia.

The processes of the defects generation under mechanical dispergation 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 dispergation time in the ball-mill planetary activator and the redistibution of impurities throughout the crystal lattice, accompanied by the formation of their complexes with the dislocations. The physicochemical modelling of the effect of fractionalization of impurities into imperfect crystals by computer (Tauson & Akimov, 1992) showed that cesium 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 submicroscopic structural changes obtained by the Fourier analysis of diffraction line profiles. After a lapse of dispergation 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.


PS11.04.09 INVESTIGATION OF KINETIC OF DEHYDROXYLATION REACTION IN MUSCOVITE. M. Dehtyaruk, E. A. Kalinichenko, A. S. Litovchenko, A. M. Kalinichenko, N. N. Bagmut, Institute of Geochemistry, Mineralogy and Oreformation, Ukrainian Academy of Sciences, Palladina pros., 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 dependencies 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 π-π INTERACTION TO π-COA­VALENT BOND. T. Ishida,*, Y. In,*1, H. Nagata,*, C. Hayashi,*, M. Doi, and A. Wakahara*1 C*2Department of Physical Chemistry, Osaka University of Pharmaceutical Sciences, 2-10-65 Kawai, Mutsukara, Osaka 580, Japan, *2Fujisawa Pharmaceutical Co., Ltd., 2-1-6 Kashima, Yodogawa-ku, Osaka 552, 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 ~2.5 Å between the =C=CH=N–C=H= fragments of the centrosymmetricallyrelated Schiff bases, which correspond to an intermediate distance of the intermolecular π–π short contact and the usual σ-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 Sp² → Sp² 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 Schiff base (cf. Chu, N., Ishida, T. & Ohtani, C. [2012] J. Am. Chem. Soc. 134, 17124-17127) (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.