

Таким образом, методом математического моделирования рассчитан равновесный состав системы “ $\text{H}_2\text{O} - \text{H}_2\text{SiF}_6 - \text{пиперидин}$ ” с участием различных ионно-молекулярных форм гексафторосиликат-иона и азотсодержащего органического основания – пиперидина.

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QUANTUM CHEMICAL MODELING OF MEERWEIN REACTIONS. THE ROLE OF THE TRIPLET STATE OF ARENDIAZONIUM SALTS AND SPIN CATALYSIS

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Diazonium salts, $\text{YArN}_2^+ \text{X}^-$, where Ar is aryl residue with substituent Y and X is a complex anion of low nucleophilicity, are starting reagents in Meerwein condensation reactions (chloroarylation of unsaturated compounds). have been investigated for a number of Y and X species by density functional method (DFT) with account of solvent effect by polarized continuum model (PCM). Dielectric permeability of solvent was chosen in the interval from water to acetone. Calculation of these salts in vacuum (with anions $\text{X}=\text{Cl}^-$, Br^-) provide pure covalent bound compounds with low polarity of the N-X bond. In water the phenyl diazonium salt is characterized by a large N-X distance (3.1 Å) and strong polarization. These salts have received remarkable attention as the first efficient photoinitiators for cationic polymerization [1]. In general diazonium salts are very unstable and it is difficult to extract them from water solvents. A poor thermal stability of diazonium salts often limits their use as photoinitiators for polymerization. The 4-alkyloxysubstituted diazonium salts ($\text{Y} = \text{OC}_6\text{H}_{13}$) with complex anion of low nucleophilicity ($\text{X} = \text{BF}_4^-$, PF_6^- , SbF_6^-) are pretty stable in several solvents and have a good photosensitivity to UV light (315 nm).

Photolysis of the diazonium salts produces paramagnetic species which EPR spectra and hyperfine structure which are typical for both diazenyl and aryl radicals [1]. The photolysis of the diazonium salts in the presence of vinyl ethers and epoxides is accompanied by the oxidation of the monomer. Moreover, the photo-induced electron transfer starts the Meerwein-reduction of the diazonium salts, which is usually catalyzed by CuCl_2 in thermal reactions. Aryl radicals can be formed also from aryl cations in the triplet state [2]. EPR measurements prove that a second radical source exists in an oxygen saturated vinyl ether solution under irradiation; this is charge-transfer complex formation [1]. In order to check these mechanisms we have calculated by time-dependent DFT the excited states of a number of aryl-diazonium cations. Their geometries were optimized in the ground and excited states, including the reduced radical forms. Comparison of the Meerwein reaction of the diazonium salts catalyzed by CuCl_2 in thermal reactions with the mechanism of photo-induced cationic polymerization lead us to idea of the diazonium triplet state involvement into the mechanism of the former thermal process. This is in agreement with general ideas of spin-catalysis concept [3].

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