**AB INITIO QUANTUM CHEMICAL STUDY OF THE REACTION MECHANISM OF ETHYNIDE ION FORMATION IN THE **C**₂**H**₂/MOH/DMSO SYSTEM (M = Li, Na, K)**

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The reaction mechanism of the formation of alkali metal ethynides C₂H₂ + MOH → C₂HM + H₂O (M = Li, Na, K) is studied for the gas phase (MP2/6-311++G***/RHF/6-31+G*) and also with regard to the solvent effect of dimethyl sulfoxide (DMSO) included within the continuum model. Among all acetylene complexes with alkali metal hydroxides considered (C₂H₂-MOH (M = Li, Na, K)), only the complex with KOH is thermodynamically stable in DMSO solution. The formation of this structure results in activation of the acetylene molecule towards electrophilic attack. The formation of alkali metal ethynide in solution is also thermodynamically favorable only in the system with potassium hydroxide of a whole series of metals considered. Further, the ethynide ion can interact in HCCK-HOH systems.

**Keywords:** ethynide ion, ethynylation, reaction mechanism, quantum chemical calculation, superbasic media.

**INTRODUCTION**

The systematic use of superbasic catalysts and reagents has enabled both to discover principally new ways of synthesis based on acetylene (for example, synthesis of pyrroles) and to improve the most important acetylene reactions catalyzed by bases: vinylation, ethynylation, and triple bond prototropic shift [1, 2]. The main limiting parameters of classic reactions are the pressure of acetylene vapors, relatively high temperature, and sometimes the application of explosive catalysts. These problems hindered the technologization of the processes and imposed serious restrictions on the structure of compounds formed due to the high temperature synthesis. The use of catalytic media with increased basicity radically changes the situation because under these conditions most processes involving acetylene proceed at atmospheric pressure and a temperature lower than 100°C [1, 2]. Media with increased activity of anions and consisting of a strong base and a solvent or reagent capable of specific binding of the cation are considered as superbases [3].

Ethynylation reaction discovered by Favorskii, whose classical variant is the condensation of ketones and aldehydes with acetylene in the presence of bases, mainly potassium hydroxide, is actively applied in organic synthesis [4]. Among the products of this reaction, propargyl alcohol and 1,4-butynediol are very important. Until recently, the classical synthesis of propargyl alcohol was performed in the presence of explosive catalyst (copper ethynide) under increased pressure and temperature [1]. A new technology of the process has recently been developed. The use of superbasic KOH/DMSO system to

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catalyze this reaction allows the synthesis to be performed under atmospheric pressure and room temperature. And if necessary, it is possible to obtain only propargyl alcohol with a yield of 95% [2, 3].

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\text{(CH}_2\text{O})_n + \text{HC}≡\text{CH} \xrightarrow{\text{KOH/DMSO}} \text{OH}
\]

Ethynylation of aldehydes and ketones is considered as addition of ethynide ions to the triple bond. Then one of the conditions of this reaction is the formation of the active \([\text{C}_2\text{H}_3^-]\) anion. Acetylene complexes with alkali metal hydroxides \(\text{C}_2\text{H}_2\cdot\text{MOH}\) can be precursors for the formation of ethynide ions. These structures are supposed to be key ones in the presence of superbases because the reactivity of acetylene increases [1-3]. Tedeschi [5] has experimentally isolated and characterized the complexes of this composition. Theoretical quantum mechanical studies performed previously have showed that acetylene can form complexes with cations of alkali metal hydroxides that have the T-structure [6].

In this work, we have examined the structure of acetylene complexes with alkali metal hydroxides \(\text{C}_2\text{H}_2\cdot\text{MOH}\), where \(\text{M} = \text{Li}, \text{Na}, \text{and K}\). The mechanism of the formation of alkali metal ethynides \(\text{C}_2\text{HM}\) in the \(\text{C}_2\text{H}_2/\text{DMSO}/\text{MOH}\) medium (where \(\text{M} = \text{Li}, \text{Na}, \text{and K}\)) is analyzed for the gas phase and the solvent (DMSO) as well as the effect of the alkali metal nature on the course of the process.

**CALCULATION PROCEDURE**

A preliminary study of potential energy surfaces (PES) for the gas phase was carried out in the framework of the restricted Hartree–Fock method with the 6-31+G* basis set, and then the energy was refined in the MP2/6-311++G**//RHF/6-31+G* approximation using the GAMESS [7] and Gaussian-98 [8] programs. For all stationary points the number of negative eigenvalues of the Hessian matrix was analyzed; the connection between the transition states found and the corresponding minima on the PES was proved by descending along the reaction coordinate using the Gonzalez–Schlegel algorithm [9]. The results presented with regard to solvation effects were obtained with the use of a combined calculation procedure [10, 11]. For the stationary points obtained in the RHF/6-31+G* approximation in the gas phase the spherical cavity radius was determined for subsequent calculations within the Kirkwood–Onsager model, a variety of the self-consistent reaction field (SCRF) models [12, 13]. Further geometry refinement in DMSO solution was performed within the density functional method with the hybrid B3LYP functional [14, 15] and 6-31+G* basis set. At this stage of the calculation, the solvent effect was taken into account within the SCRF model. In the same B3LYP/6-31+G*, SCRF approximation, vibrational corrections were calculated. Then the energy of stationary points were refined in the extended 6-311++G**//B3LYP/6-31+G*).

The solvation energy in DMSO was calculated within the polarizable dielectric model in the integral equation formulation of the polarizable continuum model (IEFPCM) [16]. To describe the cavity, we used the recommended [17] radii of spheres for C, O, and H atoms and 1.00 (Li), 1.25 (Na), and 1.60 (K) radii [19] obtained for alkali metal atoms based on the united atom topological model (UATM) [18] with a common scaling factor of 1.35 for DMSO.

**STRUCTURE OF COMPLEXES OF THE ACETYLENE MOLECULE WITH ALKALI METAL HYDROXIDES \(\text{C}_2\text{H}_2\cdot\text{MOH} (\text{M} = \text{Li, Na, and K})\)**

According to RHF/6-31+G* calculations for the gas phase, the formation of complexes \(\text{I}\) of alkali metal hydroxides with the acetylene molecule (\(\text{H}^{(i)}\text{C}^{(2)}\text{C}^{(3)}\text{H}^{(4)}\cdot\text{MOH}\)) is thermodynamically favorable. The formation energies of \(\text{I}\) are close and