Journal of Structural Chemistry, Vol. 48, Supplement, pp. S100-S110, 2007
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AB INITIO QUANTUM-CHEMICAL STUDY OF VINYLATION OF PYRROLE AND 2-PHENYLAZOPYRROLE WITH ACETYLENE IN A KOH/DMSO SYSTEM

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UDC 539.193+547.741+541.124

Interaction between pyrrole and its 2-vinyl, 2-azo, and 2-phenylazo derivatives with acetylene in the gas phase and DMSO was studied using the MP2/6-311++G**//MP2/6-31G* ab initio approach and including the solvation effects within the framework of the continuum model. Possible reasons are considered for the hindered character of direct vinylation of azopyrroles with acetylene in superbasic media. The introduction of the azo group in the 2 position of the pyrrole ring leads to the increased stability of the pyrrole anion and increased acidity from $pK_a = 22.1$ for pyrrole and $pK_a = 20.5$ for vinylpyrrole to $pK_a = 16.6$ and 16.4 for 2-azopyrrole and 2-phenylazopyrrole, respectively. The binding energy between the pyrrole anion and the acetylene molecule decreases concurrently. The heat of formation of the pyrrole anion adducts with acetylene changes from $\Delta H = 4.8$ kcal/mol for pyrrole to $\Delta H = 22.4$ kcal/mol for 2-phenylazopyrrole. For all anion adducts under study, preferable isomers are *Z* isomers formed by the interaction of pyrrole anions with the *cis*-distorted acetylene molecule, but the formation of the *E* isomers corresponds to a lower activation barrier, which explains known *Z* stereoselectivity of the nucleophilic addition to monosubstituted acetylenes. When an azo group is introduced, the reaction becomes more endothermal, and the energy barriers to the formation of both *Z* and *E* isomers increase. Among other reasons for lowering of the activity of 2-arylazopyrroles during vinylation we consider possible reaction of acetylene addition at the most remote nitrogen atom of the azo group and participation of the anion center in cation chelation (K^+ in the calculation).

Keywords: acetylene, pyrrole, 2-phenylpyrrole, vinylation, *N*-vinylpyrroles, anions, mechanism, *ab initio* calculation.

INTRODUCTION

Aryl- and hetarylazopyrroles have recently attracted attention as promising compounds for the creation of new materials [1-12]. Their molecules contain deeply polarized and easily polarizable push-pull electron systems, which make them promising in design of materials for nonlinear optics. Introduction of the vinyl group in the pyrrole ring, in particular, at the nitrogen atom permits one to substantially increase the potential of these compounds by converting them into monomers and even more reactive building blocks for selective synthesis of highly technological materials. Poly-*N*-vinylazopyrroles,

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