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Theoretical and experimental study of 2-methylimidazole formation

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The interaction of mono- and dicarbonyl compounds with ammonia and amines leads to the formation of a valuable class of aromatic compounds, namely, imidazoles. These a liquid-phase processes underlie the synthesis of most nitrogen-containing heterocycles. These heterocycles are widely used in all fields of science and life, including the development of a new generation of drugs and production of polymers. These compounds are also a part of insecticides and various dyes.

The methods of synthesis of imidazoles are mainly described in patent literature. In this paper, we are focused on the synthesis of imidazoles by the Debus-Radziszewski method [1, 2], i.e. the interaction of α-dicarbonyl compounds with ammonia and aldehydes, in particular, the reaction of glyoxal with ammonia and acetaldehyde to form 2-methylimidazole [3, 4]. The accurate data on the mechanism as well as thermodynamic and kinetic regularities of this process have not been found in the literature. At present, the reaction of acetaldehyde with ammonia [5] and the reaction of glyoxal with ammonia [6] in the aqueous medium are studied separately. The products of such interactions are identified. In the case of acetaldehyde–ammonia interaction, 2,4,6-trimethyl-1,3,5-hexahydrotriazine is a reaction product, while in the case of glyoxal–ammonia system, a series of equivalent C–N oligomers containing imidazole rings are formed. The mechanisms of these processes were suggested, their kinetics was studied by various methods of physical-chemical analysis.

Thus, the present work is aimed to determine the mechanism, kinetic and thermodynamic parameters of the 2-methylimidazole formation process by quantum chemical calculations combined with experimental data obtained using NMR spectroscopy.

In the present work, the schemes of the interactions between intermediates of acetaldehyde–ammonia and glyoxal–ammonia interactions resulting in the formation of 2-methylimidazole by the Debus method are proposed. A complete analysis of the potential energy surface (PES) of these mechanisms was carried out. A regular series of intermediate compounds participating in the most favorable pathway of the aromatic product formation are determined.

The calculations were carried out using the Gaussian'09 software package at the B3LYP/6-311G (d,p) level of the theory. The total free energy of the system in solution, taking into account solvation (PCM method), was used to construct the potential energy surfaces (PES). The solvation energy includes electrostatic and non-electrostatic contributions.

The kinetic data of the formation of 2-methylimidazole in the reaction of glyoxal and 2,4,6-trimethyl-1,3,5-hexahydrotriazine (adduct of acetaldehyde and ammonia) in water solution as well as data on the structure of possible intermediates were obtained by the method of NMR spectroscopy.

References

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