

OXIDATION OF 8-OXYQUINOLINE BY PERACIDS IN VARIOUS ORGANIC ENVIRONMENTS*Kachmaryk V. V.*, Nahorniak I. M., Kovalskiy Ya. P., Dutka V. S.Ivan Franko National University of Lviv, Kyrylo&Media Str., 6, Lviv 79005, Ukraine
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Oxidation of aromatic N-heterocyclic compounds by peroxy acids (PAs) results in the formation of N-oxides and the corresponding carboxylic acid. The reaction rate is affected by the environment in which the oxidation process is conducted. In inert solvents, PA molecules exist in the form of five-membered intramolecular hydrogen bonds. Reaction media capable of intermolecular hydrogen bonding will alter the reactivity of the PA. An 8-oxyquinoline (8OQ) molecule can also form an intramolecular bond between the OH group hydrogen and the nitrogen atom. Conformational analysis of 8OQ and PA molecules was performed and the energies of intramolecular hydrogen bonds were calculated.

In our work, the kinetics of 8OQ oxidation by peroxidecanoic acid (PDA) in a solution of acetone, benzene, and other organic solvents were studied. The kinetics of the oxidation reaction is well described by the first-order kinetic equation. The calculated rate constants for the oxidation rate of 8-oxyquinoline by PDA in benzene are higher than in acetone. Because acetone can interact with PDA and 8OQ to form intermolecular hydrogen bonds, the reactivity of both reagents is substantially altered. The reaction mechanism involves the rapid formation of the 8OQ-PA complex, which decomposes in the second stage to form N-oxide and the corresponding carboxylic acid. According to the temperature dependence of the effective rate constants of the oxidation reactions obtained in different solvents, the activation energy E_a of the process was calculated. The numerical values of E_a are in the range of 15.6–57.4 kJ/mol and are close to the numerical values of the oxidation processes. The thermodynamic parameters of the activated state (ΔH^\ddagger , ΔS^\ddagger , and ΔG^\ddagger) are calculated. There is a linear relationship between the values of ΔH^\ddagger and ΔS^\ddagger indicating that there is a compensating effect.

Molecular modeling of the investigation reaction is of considerable interest. Semi-empirical methods using Mopac2016 software and the Winmostar 9.4 GUI were calculated for the reacting molecules and reaction products: heat of formation (ΔH^f), volume (V) and area (S), dipole moments (μ).

According to quantum-chemical calculations, the molecule 8OQ and its N-oxide are flat. The geometrical parameters of the molecules were found and the partial charges on the atoms were calculated. The heat of formation of PAs with the content of carbon atoms from 1 to 12 and their corresponding carboxylic acids was calculated. The dependence of the heat of formation on the number of carbon atoms in the molecule for both acids and their corresponding PA is linear. According to the Hess equation, the heat of reaction of the oxidation of 8OQ with peroxy acids was calculated. The calculated values of the formation heat are in good agreement with the NIST thermochemical data.