Relation between electrochemical properties and quantum-chemical parameters of antipyrine and its derivatives

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Nowadays antipyrine and its halogen-derivatives (especially iodine-antipyrine) are widely used in medicine as antiphlogistic species. Iodine-antipyrine shows to be effective for prophylactic purposes against flu and other infections. Investigation of the relation between electrochemical properties and structures of these compounds seems to be very interesting problem. It could be a key to comprehension of mechanisms of biochemical oxidation of these substances in tissues.

Data of distribution of electronic density over the molecule structure (figure 1) would allow to determine active atoms groups, which are responsible for oxidation of whole molecule. On the other hand, oxidation electrode potential of the substance is important thermodynamic property determining oxidation process. Moreover, investigation of the relation between quantum-chemical parameters of the substance and its electrochemical properties would predict various substance characteristics [1].

Properties of antipyrine and its chlorine-, bromine-, iodine-derivatives have been investigated in this work. The structure formulas of these compounds are indicated in the table I.

Electronic structure of investigated molecules has been calculated using semiempirical method AM1. This method permits to make quantum-chemical calculations of energy of high occupied molecular orbital (HOMO) E_{HOMO}, difference of formation heats of a molecule and its cation radical $\Delta\Delta H$.

Oxidation potential is one of the main electrochemical properties of any substance. Potentials of anodic oxidation of antipyrine and its halogen-derivatives have been determined by voltammetry. This method involves the recording of voltammograms of the anodic oxidation of the substances by means of voltammetric analyzer connected with electrochemical cell, which consists of the working carbon glass microelectrode, silver/silver chloride reference electrode and a nitrogen supply tube. Supporting electrolyte was 0.1M Na_2HPO_4 in aquatic-ethanol medium.

Oxidation potentials of investigated substances are indicated in the table I. Comparative analysis of these data shows that the more the oxidation potential of substance, the more the difference of formation heats of the molecule and its cation radical ($\Delta\Delta H$) and the less the energy of HOMO.

Moreover, curves of the oxidation current of the investigated substances against their concentration in the solution have indicated maximum values for $C=6\cdot10^{-4}$ M. This fact could be expect a mechanism of dimerization of the substances for oxidation [2]. Distributions of electronic density over the molecular structures of antipyrine (figure 1) and its derivatives have shown obtaining of dimer after cation-radical formation by eliminating halogen (-Cl, -Br, -I) or hydrogen (in the case of antipyrine) from molecule.

Thus, results of this work allow to determine the relation between quantum-chemical parameters and electrochemical properties of the substances by example antipyrine and its derivatives. The possible oxidation mechanism of these compounds has been suggested. The results of the work could be used for investigation of mechanisms of antiphlogistic action of these pharmaceuticals in the human organism.

1. V. D. Philimonov, Yu. A. Karbainov, E. I. Korotkova, N. V. Bashkatova//J. Izv. Un. (Russia). 2002, Vol. 45, p. 75-79.
2. James F. Ambrose, Lawrence L. Carpenter, Robert F. Nelson//J. Electrochem. Soc. 1975, Vol. 122, p. 876-893.

Fig. 1. Distribution of electronic density over the molecule of antipyrine

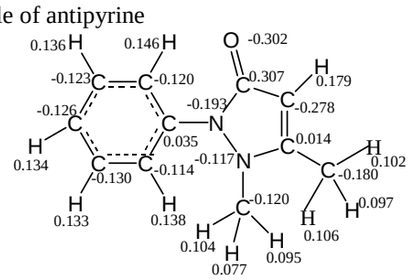
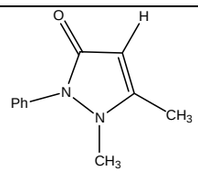
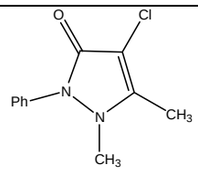
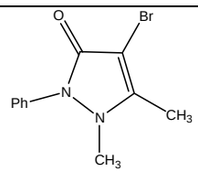
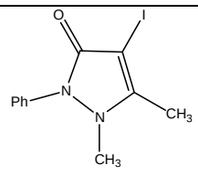


Table I. Oxidation potentials (E) and calculated values of energy of HOMO (E_{HOMO}) and differences of formation heats ($\Delta\Delta H$) for antipyrine and their halogen-derivatives

Structure of compounds	E, V	E_{HOMO}, eV	$\Delta\Delta H$, kDg/mol
 antipyrine	1.11	-9.02	766.0
 chlorine-antipyrine	1.14	-8.84	787.8
 bromine-antipyrine	1.12	-8.89	787.0
 iodine-antipyrine	1.05	-8.89	784.0