Thematic Section: Kinetics and Catalyses. **Analytical Review**
Subsection: Structural Chemistry. *Registration Code of Publication:* 10-23-14-43
Publication is available for discussion in the Internet as a material of "All-Russian Working Chemical Conference "*Butlerov's Heritage-2011*". http://butlerov.com/bh-2011/
Contributed to editorial board: November 11, 2010.

Kinetics and mechanism of the chain reversible reactions in quinoneimine + hydroquinone systems

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Keywords: *quinoneimines, hydroquinones, semiquinone radicals, chain reversible reactions, kinetics, mechanism, rate constants, bond dissociation energies.*

Abstract

The progress in studying the kinetics and mechanism of reversible chain reactions in the systems quinoneimine + hydroquinone – the first chain reversible reactions in liquid phase that follow the "classic" kinetics scheme have been reviewed. The mechanism of the reactions as well as the experimental rate constants of the elementary steps with the participation of the semiquinone radicals has been revealed. The dual (accelerating and retarding) effect of the final products on the kinetics of the reactions have been discussed; the latter proves the pronounced reversible nature of elementary stages of these chain reactions. Direct experimental evidences have been presented proving the reversible nature of the chain reactions in the systems quinoneimine + hydroquinone obtained in a study of the reaction of *N*-phenylbenzoquinoneimine with 2,5-dichlorohydroquinone when the same equilibrium state has been reached by the chain mechanism (proved by adding initiator to the system) from the starting materials as well as the reaction products. It has been noted that the rate constants of elementary steps in conjunction with the method of intersecting parabolas allowed to determine for the first time the strength of HO- and NH-bonds in the 4-hydroxydiphenilamine and several semiquinone radicals. It is shown that the data on the kinetics of reversible chain reactions in quinoneimine + hydroquinone systems can be used as a method of studying the influence of the media and the structure of the reagents on the reactivity of semiquinone radicals.