

## Determination of rate constants for disproportionation of 2,5-dichlorosemiquinone radicals by the laws of non steady state kinetics of chain reactions

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### Abstract

Two variants of the new method of determining the rate constants for disproportionation of semiquinone radicals  $k_6$  by the laws of chain reactions of quinoneimines with hydroquinones under nonstationary conditions are developed. Unsteady state is provided by accumulation of semiquinone radicals or radical initiator prior to the reaction in a higher concentration as compared to the stationary concentration of semiquinone radicals in the chain reaction. Variants of the method differ from each other in the nature and concentration of the radicals accumulated in the system before starting the reaction, which is provided by different order of mixing reagents and initiator. In the first case before the reaction initiator solution was prepared with the hydroquinone (semiquinone radicals are accumulated), to which quinonediimine is added (start of the reaction). In the second variant the initiator solution was prepared with the quinonediimine (initiator radicals are accumulated), to which hydroquinone is added (start of the reaction). The dependence of quinonediimine concentration decrease for some short time ( $\sim 20$  sec.) after the start of the reaction on the rate of initiation is used to determine the  $k_6$ . With the use of the new method there was determined for the first time the rate constants for the disproportionation reaction of 2,5-dichlorosemiquinone radicals in weakly polar chlorobenzene ( $k_6 = (3.0 \pm 0.5) \times 10^6 \text{ l mol}^{-1}\text{s}^{-1}$ , where only one variant of the method) can be realized, a non-polar benzene ( $k_6 = (5.0 \pm 2.2) \times 10^6$  (first variant) and  $(7.3 \pm 3.7) \times 10^6 \text{ l mol}^{-1}\text{s}^{-1}$  (second variant) and decane ( $k_6: (1.1 \pm 0.4) \times 10^8$  (first variant) and  $(0.8 \pm 0.1) \times 10^8 \text{ l mol}^{-1}\text{s}^{-1}$  (second variant).