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Kinetics of the thermal decomposition of 2,2'-azobis(2-amidinopropane)dihydrochloride in an aqueous solution of 1,4-dioxane

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Abstract

With the aim of developing a method of quantitative research of water-soluble oxidation inhibitors studied thermal decomposition of water-soluble initiator 2,2'-azobis(2-amidinopropane) dihydrochloride in water solution of 1,4-dioxane. 2,2'-Azobis(2-amidinopropane) dihydrochloride is highly soluble in water, where monomolecular decomposes with formation of free carbon-centered radicals, which rapidly react with oxygen to produce peroxyl radicals, initiating a radical chain process. The role of substrate oxidation applied 1,4-dioxane, solvent was water. In this system, the thermal stability of 2,2'-azobis(2-amidinopropane) dihydrochloride have not been studied previously. Were obtained optical absorption spectrums of 2,2'-azobis(2-amidinopropane) dihydrochloride in water and in water-dioxane solution. It is shown that the maximum absorption is observed at a wavelength of 366 nm, the value of the extinction coefficient both in aqueous and in water-dioxane solution is 24.4 ± 3.0 $mol \cdot l^{-1} \cdot cm^{-1}$.

The data about thermal decomposition of 2,2'-azobis(2-amidinopropane) dihydrochloride was obtained by measuring the initiated oxidation rate of 1,4-dioxane in aqueous solution. The oxidizing agent was the oxygen from the air. With the reaction rate was monitored by manometric method at the appliance, equipped with a differential pressure transducer that records changes in pressure in the gas phase. Using the value of the coefficient of Henry for oxygen solubility in 1,4-dioxane, calculated the change of oxygen concentration in the liquid phase. Studied kinetic characteristics of the radical-chain oxidation of 1,4-dioxane in the water medium. It is established that at a temperature of 333 K, the rate of oxygen consumption during the oxidation of 1,4-dioxane initiated with 2,2'-azobis(2-amidinopropane) dihydrochloride, increases with increasing concentration of 1,4-dioxane (RH) and concentration of initiator (ABAP). The observed correlation between the oxidation rate w and parameters $[ABAP]^{0.5}$ and [RH] is linear. At the same time, the oxidation rate of 1,4-dioxane is not dependent on oxygen concentration. Therefore, oxidation of 1,4-dioxane in aqueous solution proceeds via radical-chain mechanism with quadratic-law chain termination and the oxygen absorption rate is expressed by the equation: $w = k_2 \cdot k_6^{-0.5} \cdot [RH] \cdot (k_i[ABAP])^{0.5}$.

Using the values of the 1,4-dioxane oxidizability($k_2 \cdot k_6^{-0.5} = 3 \cdot 10^{-4}$ $l^{0.5}$ $mol^{-0.5}s^{-0.5}$, 333 K) and considering the fact that 2,2'-azobis(2-amidinopropane) dihydrochloride, the yield of radicals in volume in aqueous solutions is ~0.5, the rate constant for decay of 2.2-azobis(2-amidinopropane) dihydrochloride in the system 1,4-dioxane-water=1:1 (v/v) is $(3.6 \pm 0.6) \cdot 10^{-5}$ s^{-1}.

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