

Kinetics of hydrogen peroxide consumption of the oxidation dimethyl sulfoxide in the presence of tungstic and molybdic acid

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Abstract

Kinetic regularities the consumption of hydrogen peroxide in the oxidation reaction of model compound – dimethyl sulfoxide were studied. It is shown that the rate of consumption of hydrogen peroxide in the presence of tungstic or molybdic acid decreases with time. The experimental data is presented in the form of kinetic equations describing the expenditure of hydrogen peroxide. On the basis of the equation and the experimental data were calculated effective rate constant of consumption hydrogen peroxide at 353 K.

Kinetic analysis of experimental data allowed us to propose the scheme of the catalyzed peroxidation reaction of dimethyl sulfoxide. Upon dissolution of molybdenum or tungsten acid in hydrogen peroxide formed the peracids further in equilibrium stages – diperasids. The accumulating diperic acid form a complex with dimethyl sulfoxide, by the decay which is forming peracid and dimethyl sulfone. The proposed scheme with considering experimental data allowed formulating the main factors determining the technological mode of the oxidation process. Technological mode of process must be selected such that the rate-limiting step of the process was the disintegration sulfoxide complex with diperic acid. The rate of other stages that presented in scheme should exceed the rate of decay complex of dimethyl sulfoxide and diperic acid. In experiments were using soluble homogeneous catalysts which are pre-incubated for 30 minutes in the hydrogen peroxide that the rate of formation of peroxy and diperoxy acids when catalyst reacting with the hydrogen peroxide is not to limit the oxidation process. During this time were formed peroxy compounds of catalyst and the equilibrium concentration of these oxidizing agents in reaction was maintained. It was established experimentally that the rate of oxidation is proportional to the square of the concentration of hydrogen peroxide, and therefore the content of hydrogen peroxide in the reaction system should provide a fairly rapid consumption of the reagent. It was found that necessity to maintaining the desired concentration dimethyl sulfoxide and diperic acid in reactor that the diffusion rate of reactant molecules didn't become limiting in this process.