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A Theory of Accumulation of Frozen Radicals in Solids

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A study of five different models—to describe the mechanism of accumulation of free radicals produced in low temperature irradiation of solids—resulted in formal kinetic expressions for each model. This mechanism is linked to the transfer of charges, mobil atom migration, excitation transference, and thermal wave diffusion. These formal kinetic expressions for each of the models are compared with the experimental low-temperature free radical accumulation data for a number of compounds. The comparison shows that, except for the case of frozen radical accumulation at temperatures close to that of liquefied helium, none of the models yields adequate quantitative expressions for the limiting free radical concentrations.

Kinetics of Consumption of Oxidation Inhibitors Introduced at the Start of Oxidation Reactions

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The results of a theoretical investigation are presented covering consumption of oxidation inhibitors introduced at the start of oxidation reactions. The kinetic inhibitor consumption curves shown are based on the data obtained by solving appropriate differential expressions with the aid of electronic computers.

The experimental data of consumption of α-naphthol in oxidation of cyclohexanone, tetralin, and cyclohexanol are compared with the corresponding calculated data. A new method is proposed to correlate the kinetics of peroxide accumulation and of inhibitor consumption with the rate constants of peroxide radical-inhibitor and the radical-oxidate reactions.

Use of Radioactive Mercury in Studies of Free Radicals in Solutions

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Thermal decomposition of the initiators of radical polymerization reactions in solutions was studied using an indicating reaction method, which is described. This method is based upon interaction of mercury with the free radicals formed. Pertinent experimental data confirm the validity of theoretical conclusions regarding the indicating reaction mechanism and point to possible applicability of this technique in studies of diazoaminobenzene and diphenyl mercury. Studies of decomposition of diphenyl mercury with the aid of combined spectrophotometric and indicating reaction analytical methods disclose presence of the exposure cage effect.

Technical Synthesis of Carbonyl Monomers Based on Mannich's Reaction

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The kinetics of interaction of propionaldehyde, acetone, and methyl ethyl ketone with formaldehyde and diethylamine was investigated using Mannich's reaction. The results show that the rates of these reactions are greatly affected by pH of the reacting medium. For propionaldehyde, the rate increases with increasing pH; for acetone and methyl ethyl ketone, the reverse is true.

Kinetics of the reactions at pH values corresponding to high reaction rates are expressed by the third order equations. The reaction rate-temperature correlations and the corresponding calculated activation energy values are shown. Additional information regarding Mannich's reaction mechanism is also presented.