tion" (Chapter 4). Then the mechanism of stereoregulation in the polymerization with a metal alkoxide catalyst has been studied. Some observations presented here support the assumption that the stereoregulation is performed by the steric hindrance around the catalyst sites, which are controlled primarily by the bulkiness of the alkoxy group and by the degree of catalyst aggregation (Chapters 5 and 6). Polymerization by $Al(C_2H_5)_3$–H_2O systems (Chapter 7) with varying $H_2O/Al(C_2H_5)_3$ ratios and the alternating copolymerization of acetaldehyde with trichloroacetaldehyde by the $Al(C_2H_5)_3$ catalyst (Chapter 8) have also been described.

Abstracts of Articles in Russian Journal, "Kinetics and Catalysis," Volume 6, Number 2, pages 185–195; Published by Siberian Division of the Academy of Sciences of USSR

Chemiluminescence in Slow Chemical Reactions: Application to Studies of Kinetics of Gaseous Phase Oxidation Reactions

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Studies show that the chemiluminescence in oxidation of different organic compounds is quenched by oxygen. Since, here, oxygen functions as a reactant and a quenching agent, the kinetic curves of the chemiluminescent reactions at small concentrations of oxygen typically pass through a maximum point. In oxidative decomposition of tertiary butyl peroxide (TBP) and in oxidation of acetaldehyde, the time to reach the respective maximum points was utilized to determine kinetic parameters of the two reactions.

The results of determination of kinetics of chemiluminescence in oxidation of propane over hydrogen bromide as the catalyst show that, here, the chemiluminescence reflects the kinetics of formation and consumption of an unstable intermediate reaction product.

Reactivity of Phosphoric and Thiosulfuric Acid Esters with Cholineesterase and Hydroxyl Ions

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Reactivity of phosphoric and thiosulfuric acid esters ("POS") was studied in inhibited cholineesterase (CE) and hydrolysis reactions. For these reactions the rate constants were determined and the pre-exponential factors were calculated. It was found that the kinetic constants vary with changes in the structure of "POS."

Nature of Intermediate Radicals Formed in Inhibited Radical Polymerization Reactions

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Pictures were taken of the EPR spectra of the radicals produced in polymerization of styrene in presence of the reaction-inhibiting compounds resulting from addition of a macro-radical to certain aromatic nitroso-compounds.

The basic characteristic of the spectra of the intermediate radicals, in which a nitroso-group is attached to the benzene nucleous, is the triplet of 1:1:1 intensity ratio, involving splitting of 10–12 electrons. The triplet is formed by interaction of the unpaired electron with the nitrogen-containing nucleous. With the radical concentration measurements as the basis, correlations between some of the constants were evaluated for the elementary reactions.

Mechanism and Kinetics of Bromination of Vinylphosphinic Acids

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The mechanism of bromination of derivatives of vinylphosphinic acids was studied, using the diethyl ester as an example. The results show that the reaction is of the radial type and of 3/2 kinetic order.

The bromination rates of a number of derivatives of vinylphosphinic acids were determined. The study shows that the rate constants are defined by Hammett's equation, when using the earlier-determined values of σ for the phosphorus substituent.

γ-Radiolysis of Methanol

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The action of γ-radiation of Co^{60} on methyl alcohol was determined. The results show that the yields of hydrogen, methane, and of the sum of ethylene glycol and formaldehyde increase with the temperature. Activation energy of the reaction is 0.65 kcal/mol. The yields of dimethyl ether and of formaldehyde decrease with increasing reaction temperature.

Addition of certain compounds to methanol being irradiated appreciably increases formaldehyde yields.

The results obtained are explained in the light of the concepts for diffusion processes.

Formation and Reactions of Free Radicals in Ultraviolet Irradiation of Organosilicones: Silazanes

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EPR and mass spectral analyses were made of the gaseous products of interaction of the radicals formed in irradiation by ultraviolet light of certain silazanes at a temperature of 77°. The results show that formation of the free radicals occurs by rupture of the Si—C, Si—H, and C—H chemical bonds.

Kinetics of Hydrogen Adsorption on Al_2O_3 by γ-Irradiation

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A study was made of kinetics of radiative chemisorption of hydrogen gas on γ-Al_2O_3. Equations were derived which satisfactorily describe the reaction mechanism. The number of surface centers active in the chemisorption was determined. A mechanism is suggested for the chemisorption of hydrogen at a temperature of ~300°K.

Electronic State of Catalysts in Adsorption and Catalysis: Mechanism of Hydrogenation of Carbon Monoxide Over a Nickel Catalyst

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Changes in the contact potential differences (CPD) of a nickel-chromia catalyst were determined in separate and simultaneous adsorption of H_2 and CO at the conditions directly preceding the initiation of the catalyzed reactions; the changes in CPD were also determined during hydrogenation of carbon monoxide. The results show that for hydrogen adsorption the surface charge of a catalyst sample subjected to vacuum pretreatment with hydrogen differs from that of an unpretreated sample.

The action mechanism of the nickel-chromia catalyst was examined in the light of the experimental results of the study. A scheme for hydrogenation of CO over this catalyst is proposed.

Photosorption and Photodesorption of Oxygen on Zinc Oxide: Experimental Conditions to Determine Photosorptive Properties of Muffle-Oxidized Zinc

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The study shows that after a thorough purification by preheating in oxygen, zinc oxide photosorbs oxygen exclusively. Reproducible conditions were determined for the photosorption, after saturating the catalyst by briefly heating it at a temperature of 300°–400° in vacuum or in oxygen atmosphere. The characteristic spectra were determined for the visible and near-ultraviolet regions.

By way of illustration, the results for muffle-oxidized zinc oxide show that at pressures in the range of 1×10^{-3} to 1×10^{-2} mm Hg, the amount of photosorbed oxygen is independent of the pressure but is clearly proportional to the exposure time.

Prephotoactivation of the adsorbent was uncovered.