Mechanism of Reactions Involving Proton Transfer in Polar Solvents

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Reactions of the $AH + B \rightarrow A^- + HB^+$ type are examined as consisting of a series of consecutive reaction stages, including that of the stepwise excitation of the proton oscillations in the hydrogen "bridge," A — H . . . B. The probability of this excitation, which is only randomly time-dependent, is determined with the aid of the Theory of "Disturbances." A system of kinetic equations is solved at approximated quasi-stationary conditions. The "over-barrier" and the "tunnel" courses of the reaction are considered.

Mechanism and Kinetics of HI Addition to Unsaturated Carbon-Carbon Bonds in Organic Solvents: Addition of HI to Methyl Propiolate in Chlorobenzene Solution

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The experimentally-determined rates of hydrogen iodide addition to methyl propiolate (PE) are described in terms of the bimolecular kinetic equation, $v = (k_2)(PE)(HI)$. In a temperature interval of 0°–42°, the maximum value of k_2 occurs at 31°–34°. At a temperature of 35°, k_2 is independent of the reactants concentration; at 0°, k_2 increases with concentration of the propiolic ester; at 25°, the value of k_2 is at the maximum when the reactants are present in equimolecular concentrations. The rate of HI addition to the ester is increased by adding compounds (tetrahydrofuran, methyl acetate, methanol) which form complexes with the HI molecules, instead of bonding with the hydrogen. It is concluded that the sub-acrylic ester is produced via the intermediate complex formation between the HI molecules and the carbonyl group of the propiolic ester. Participation of such a complex in the addition reaction satisfactorily explains the relationship at different temperatures between the experimentally-determined reaction rate constants and concentrations of the reactants, as well as the temperature anomalies observed.

Inhibition Studies of Mechanism of Cumene Oxidation in Liquid Phase

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The mechanism of formation of radicals from cumene hydroperoxide in cumene, chlorobenzene, and *n*-heptane media was studied by the inhibition technique, using α-naphthylamine as the inhibitor. At temperatures of 100°–140°, decomposition of the hydroperoxide in cumene onto radicals proceeds by the following route:

$$ROOH + RH \xrightarrow{k_3} RO\cdot + R'H_2O,$$

where $k_3 = 5 \times 10^7 \exp(-26{,}000/RT)$, l/mol-sec.

At a temperature of 95°, cumene hydroperoxide dissolved in *n*-heptane exists as strongly associated dimer, ROOH . . . HOOR, and at concentrations greater than 0.7 mol/l. The hydroperoxide is completely converted to the dimer form. It is via this formation of the dimer intermediate that decomposition of the hydroperoxide into radicals is realized.

In chlorobenzene solution, cumene hydroperoxide in concentrations of not over 2 mols/l decomposes along the following reaction route:

$$2\,ROOH \xrightarrow{k_2} RO_2\cdot + RO\cdot + H_2O,$$

where $k_2 = 2.4 \times 10^2 \exp(-16{,}400/RT)$, l/mol-sec.

Study of Reactivity of Macroradicals

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EPR studies were made of interaction of the macroradicals in solid-state polymers (polystyrene, polymethyl methacrylate, polyvinyl acetate) with different reactants, which effect oxidation, hydrogen split off, and addition of a monomer. The results show that the macroradicals originating from mechanical destruction of polymers dispose themselves in the vicinity of the newly-formed surface. The kinetic constants of the reactions studied were evaluated on the basis of the experimental data. The activation energy values were determined; these are significantly greater than the energies of the same reactions in liquid phase. This difference is ascribed to specificity of the solid phase reactions, where mobility of the particles is greatly inhibited.

Radio-Chemical Decomposition of $KClO_4$

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EPR studies were made of the nature of the paramagnetic centers which are produced in potassium perchlorate by exposure to ionizing radiation at a temperature of 77–450°K. The kinetics of accumulation and recombination of the paramagnetic centers at these temperatures were also investigated. The results show that recombination of ClO_2 and O_3^- radicals is a reaction of second order.

Isotopic Oxygen Exchange Over Neodymium Oxide with Different Crystal Structures

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The study of isotopic oxygen exchange was made at temperatures of 300°–500° over neodymium oxides with cubic, hexagonal, and cubic-hexagonal crystal structures. The study also covered the exchange of isotopic oxygen with the oxygen of the hexagonal-form oxide.

Activity of the oxides in isotopic oxygen exchange was found to depend on the history of their pretreatment in vacuum and in oxygen atmosphere. The crystal structure of the oxides shows no effect on their activity.

Activation energy of the isotopic oxygen exchange reaction is 30 kcal/mol and that of the exchange of isotopic oxygen with the oxide oxygen is 20 kcal/mol.

Nature of Surface Defects of Irradiated Silica Gel: Catalytic Properties of Irradiated Silica Gel in Isotopic Hydrogen-Deuterium Exchange

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Catalytic activity of irradiated silica gel was evaluated in an isotopic hydrogen-deuterium exchange reaction. The apparent energy of activation and order of the reaction were determined on the mixture partition basis. The results show that activity of the samples studied is greatly affected by the admixed aluminum concentration and by the activation and irradiation conditions. A faster method of activation was developed by tempering the samples in hydrogen atmosphere as compared to the activation by tempering in vacuum. A relationship exists between changes in the catalytic activity and the corresponding changes in the adsorption capacity for hydrogen; a relationship also exists between changes in the intensity of the sextet signals of the EPR spectra and the corresponding changes in (a) the aluminum content of the samples, (b) the conditions of activation and irradiation, and (c) the conditions of calcination in vacuum and in hydrogen media. It is concluded that in the irradiated silica gel, the "tinted" surface centers, due to the admixed aluminum, are the active centers catalyzing isotopic exchange of molecular hydrogen and adsorption of hydrogen.

Catalytic Properties of Chelated Polymers with bis-Thioamides of Quinaldene as the Carriers

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Catalytic properties of chelated polymers were investigated, using bis-thioamides of quinaldine and salts of the transition metals as the carriers. The effect of the metals and of the chain radicals on catalytic properties of the polymers was evaluated in oxidation of cumene. The results show that catalytic properties of the polymers and the reaction course are defined by the changes in electronic density on the sequestered metal and on the ligand.

Electronic Spacial and Surface Properties of Zinc Oxide

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The electronic work function, electroconductivity, and oxygen adsorption capacity of pure and modified zinc oxide were determined, using samples calcined at temperatures of 500°, 900°, and 1,300°. The results show that the electrophysical and adsorptive properties of the semiconductor are significantly affected by the preparation history. Depending on the pretreatment history, electroconductivity of the samples is either in direct or in inverse relationship with the electronic work function. A relationship was also established between the oxygen adsorption capac-