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