Polarographic Investigation of Mechanism and Kinetics of Protolytic Reactions in Nitro-Aci-Tautomeric Conversion of Nitro-Cyclohexane

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The nitro-aci dissociation and aci-nitro recombination rate constants were determined by polarographic technique in tautomeric conversion of nitrocyclohexane in presence of various proton donors and acceptors. To describe the recombination reaction kinetics in a 3 to 7 pH range requires a consideration of all possible protolytic reactions and of the aci-form molecule-anion equilibrium. At pH values of 10 to 12, the dissociation rate is primarily a kinetic function of the protolytic reaction involving participation of hydroxyl ions.

The transformations of acidic protons into aci-form anions (recombination) and of nitro-form protons into bases (dissociation) are the controlling steps in these processes.

In general, the relationship between the protolytic reaction rate constants and the dissociation constants of the corresponding acids can be expressed by Brönsted equations.

Photochemical Decomposition of Alcohols at Low Temperatures: Decomposition Kinetics of Methyl Alcohol

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The accumulation, disappearance, and mutual transformation kinetics of the radicals formed in ultra-violet irradiation of dilute solutions of H_2O_2 and C_6H_6 in CH_3OH at 77° were studied, using a direct-type resonating EPR spectrometer. Formation of the $\cdot CH_3$, $\cdot HCO$, and $\cdot CH_2OH$ radicals was uncovered. The ultra-violet light effectively decomposes the $\cdot CH_2OH$ radical into $\cdot CH_3$ and $\cdot HCO$. The concentrations of CO, CH_4 and H_2 in the gaseous end-products are 26, 17, and 57 per cent, respectively. At the conditions employed, the H_2O_2- and C_6H_6-initiated photochemical decomposition of methyl alcohol is a radical-forming process. Multiplication of free valences is one of its basic characteristics.

A Quanto-Mechanical Basis to Classify Thermal Decomposition Reactions of Solids

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The quanto-mechanical concepts can serve as a basis to classify thermal decomposition reactions of solids (ionic salts). In this classification, the Group 2 reactions involve electron migration to produce conductive zones and those of Group 1, involve transition of electrons into excited states.

Formation of Radicals in Radiolysis of Organic Solids: Yields of Radicals from Benzene and Diphenyl Derivatives

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The irradiation yields of some derivatives of benzene and diphenyl were determined by the EPR method. For the compounds investigated, the experimental G_R values are 1.5–3.0 times greater than that of benzene ($G_R = 0.2$) but significantly smaller than the values based on equation, $G_{ADD} = \gamma_A G_A + \gamma_D G_D$, where γ_A and γ_D and G_A and G_D are electron fractions and yields, respectively, of the aromatic (A) and saturated (D) groups. Probability of energy transfer from the substitute to the aromatic groups was evaluated on the basis of these experimental data. The values of energy transfer coefficients of a majority of these compounds are close to unity.

Entropies of Activated Complexes in Hydrogenation of Ethylene Over Metals

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The absolute entropy values of activated complexes produced in hydrogenation of ethylene over various metals were calculated from experimental data. The Jenkins-Rideal mechanism is not applicable to the cases of palladium and platinum. With nickel and a number of other metals, only a small portion of the surface participates in the catalysis.