Kinetics of Radiative Polymerization of Allyl Alcohol

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The data are presented for the kinetics of polymerization of allyl alcohol in cyclohexane, water, and benzene solvents, using hydroquinone, benzoquinone, etc. as the inhibitors. The degree of polymerization is evaluated with the aid of the solubility and fractionation data.

Mechanism and Kinetics of Iodization of Aromatic Amino Compounds by Iodine Chloride Dissolved in Aqueous Solutions of Hydrogen Chloride

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The rate of iodization of aniline and of metanilate and *N*,*N*-dimethylmetanilate ions by iodine chloride dissolved in aqueous solutions of hydrogen chloride, can be described by the following equation:

$$-\frac{d(\mathrm{ICl})}{dt} = \frac{k(\mathrm{M})(\mathrm{ICl})}{[\mathrm{H}^+][\mathrm{Cl}^-]^{\alpha}},$$

where M and ICL are analytically-determined concentrations of the amino compound and of the iodine chloride, and the value of α is 1.61, for aniline; 1.5, for metanilate ion; and 1.9, for the dimethylmetanilate ion. The water molecules—but not the amino compounds—serve as the acceptor of the protons being split off in the limiting step of the reaction.

Analysis of the kinetic correlations indicates that iodization by iodine chloride proceeds along two paths: (1) via formation of ClI . . . $\mathrm{ArNH_2}$) complex, and (2) via formation of (I . . . $\mathrm{ArNH_2})^+$ complex ion.

In iodization of amino compounds, the kinetic isotopic effect is greater with iodine chloride than with iodine.

Kinetics of Reaction of Phosphonitrile Chloride Trimer with Sodium Alcoholates

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A study of reaction kinetics of phosphonitrile chloride trimer (PNC) and of incomplete butyl esters of the trimer with sodium alcoholates—in different alcohols—shows that this reaction is of the first order with respect to PNC trimer, its esters, and the alkoxide ion; it is of the zero order with respect to the alcohols. The reaction rate increases with increasing dielectric constant values of the media. Increasing substitution of the chloride atoms in the butoxy-group of PNC trimer, sharply decreases the reaction rate, increases the activation energy, and lowers the activation entropy and steric factor values. The proposed probable transition state of the reaction is described.

Properties and Kinetics of Product Accumulation in Radiolysis of Benzene in Aqueous Sodium Nitrate Solutions

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Qualitative composition of the products and the product accumulation kinetics were determined in radiolysis of benzene in 0.5 *M* aqueous solution of sodium nitrate. Initially, the stable reaction products are nitrophenols, phenol, nitrous acid, hydrogen peroxide, and nitrobenzene, the latter being formed only in absence of oxygen. Radiative nitration of benzene occurs at pH values below 6.0. On the other hand, oxidation of benzene continues at pH values of over 6.0. In inert media, increasing the dosage results in conversion of nitrobenzene to dinitrobenzene and of nitrophenol to dinitrophenol. Conversion of phenol is principally via radiolytic nitration; its non-radiolytic interaction with the nitrous acid is a side-reaction, which results in formation of nitro-compounds—particularly, of nitrophenol. At pH values of over 6.0, phenol is radiolytically oxidized into hydroquinone and pyrocatechin. At pH's greater than 7.0 and high irradiation dosages, insoluble polymerization products are precipitated.

Alteration of Physico-Chemical Properties of Solids by Additives: Role of Contact Phenomena in Thermal Decomposition of Solids Catalyzed by Admixed Semiconductors

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This paper discusses probable causes of alteration of thermal stability of solids by admixed heterophase catalysts with donor-acceptor properties. In considering the causes, the character of the elementary decomposition-limiting step was taken into account. If the electronic stage is the limiting step in a reaction, the reaction rate can be altered by shifting the Fermi level of the crystalline solid being decomposed. The effect of different factors, including that of heterophase additives, on thermal decomposition of solids is considered from the above point of view. The results by the authors and by other investigators are discussed in the light of the concepts presented.

Effect of Ionizing Radiation and of Other Factors on Rate of Topochemical Decomposition of Various Inorganic Compounds

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Ionizing radiation and composition of a gaseous reactant affect differently the decomposition rates of hydroxides of magnesium and aluminum as compared to the effect of these factors on the rates of decomposition of oxalates of copper and nickel. Decomposition of magnesium and aluminum hydroxides is characterized by the presence of apparent induction periods and by the oxidation-reduction insensitivity of the gaseous media. Preirradiation of the hydroxides with γ- and β-rays has practically no effect on the subsequent course of their thermal decomposition. The decomposition of oxalates of copper and nickel is also characterized by noticeable induction periods and, in addition, by sensitivity to the oxidation-reduction properties of the gaseous media. Preirradiation of the oxalates shortens the induction periods and markedly increases the subsequent thermal decomposition rates.

Electronic (donor-acceptor) properties of the copper and nickel oxalates in the decomposition reactions are hypothesized on the basis of the experimental data of this study.

Activity and Electronic Properties of Complex Catalysts Used in Oxidation of Hydrocarbons

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Electroconductivities and electron work functions of certain mixed vanadia-molybdena catalysts were determined. Electro-physical and structural properties of these catalysts are listed alongside their selectivity characteristics in hydrocarbon oxidation reactions. The optimum component concentrations of the mixed catalysts are functions of the composition and preparation history of each system. Thus, selectivity of the mixed catalysts can be controlled by changing electronic properties of the surface via incorporation of additives with different electronegativity properties. Selectivity of the catalytic systems produced by chemical combination of the two oxides depends upon relative distribution of the metallic and oxygen ions on the catalytic surface. Finally, with the multiphase-type systems, each of the above two factors bears importantly on the catalytic selectivity.

Effect of Reactant Mixtures on Catalytic Properties of Copper Catalysts in Oxidation of Propylene

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Catalytic properties of metallic copper and of copper oxides were determined by studying the mechanism of formation of catalytically active surfaces in oxidation of propylene and acrolein. The results show that with the copper oxides, a catalytically active surface is formed by the process involving transition of CuO to Cu_2O. As a result, productivity of the catalyst increases with respect to acrolein and decreases with respect to carbon dioxide. Stabilization of catalytic activity of the copper oxide catalyst occurs faster than equilibration of its chemical composition. Selectivity of the catalyst with respect to carbonyl compounds decreases with increasing oxygen content, i.e. with increasing degree of copper oxidation.

Investigation of Nature of Irreversible Chemisorption on Semiconductors

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Interaction of chemisorbates with the additives dispersed in semi-conductive adsorbents is being investigated to determine effects of the additives on kinetics and partial irreversibility of the chemisorption reactions.

Relationship between Catalytic Properties and Electronic Structure of Iron-Cobalt Catalysts

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A relationship was established between electronic structure of iron-cobalt alloys and their