

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:

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

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 $\text{CII} \dots \text{ArNH}_2$ complex, and (2) via formation of $(\text{I} \dots \text{ArNH}_2)^+$ 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 nitrocompounds—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 crystal-