phase as the monomer. It is the nature of the active site which determines the final structure and the properties of the resulting polymer.

Kinetics of the Adiabatic Polymerization of Oligoester Acrylates

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The authors employed a thermometric technique to study the kinetics of adiabatic polymerization of oligoester acrylates, and found several specific properties of this reaction. Among them are an increase of the flexibility of the polymer matrix, and a decrease in the viscosity of the oligoester with temperature. These reaction features promote chain growth and radical termination, i.e., promote conditions approximating the steady state. This, in turn, gives polymers of higher molecular weight than those possible under isothermal conditions.

Quantitative Study on the Polar Effects of Substituents in Polymerization

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Attempts to account for the polarization effects induced by substituents on the energy of the polymerizing system gave a quantitative relationship between the rate constant for chain propagation and the polar properties of the substituents. When plotted on a Q–e diagram, this relationship contradicted the empirically derived relationships. For this reason, the author introduced a new parameter Q', which allows a more realistic separation of polar and resonance effects of the substituents on the reacting system. He then found a quantitative relationship between k_{ij} and P_i and Q_j, which allows calculation of rate constants for polymerization of all monomers from the rate constants for copolymerization (assuming that no steric effects are present).

Determination of Absolute Rate Constants for the Various Steps of a Chain Reaction by Means of Flash Photoinitiation

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The authors propose a new variant of the technique for determining the absolute rate constants of the constituent reactions of a chain process. This variant consists of measuring the rise in the temperature of the reactants (release of the heat of reaction) under adiabatic condition during flash photoinitiation. It was found that k_p/k_o for the polymerization of styrene at 20°C is 0.6×10^{-6}, while the k_p/k_o for the polymerization of acrylonitrile in dimethylformamide is 1.9×10^{-6}.

Heterolytic Rearrangement of Peresters. II. Effect of the Medium and of the Catalyst of the Reactivity of Cumyl Perbenzoate

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The rate of rearrangement of cumyl perbenzoate increases with the dielectric permittivity of the solvent. However, the permitivity effect is less pronounced than the specific solvation effect of the solvent. It is shown that in mixed solvent systems (methanol-water and ethanol-water) the log $k_{\text{rearr.}}$ increases proportionately to the ionizing power of the medium. The m_i coefficients in the Winstein-Gruwald equation are 0.39 and 0.49 for the two media, respectively. In benzene, carboxylic acids form complexes with cumyl perbenzoate. The instability constant for the cumyl perbenzoate-trichloroacetic acid complex is 0.026 at 6°C. Protonated acids and the Lewis acid $AlCl_3$ catalyze the rearrangement of this perester by increasing the polarity of the $O-O$ bond.

Effect of the Medium on the Mechanism of the Reactions of Isocyanates with Alcohols. Part II.

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Kinetic data on the reactions of isocyanates with methanol in solvents of various polarity are compared with heats of mixing of these isocyanates and methanol with these solvents. The mechanism of addition of alcohols to isocyanates in inert solvents is different from that observed in solvents capable of specific solvation of the reagents.

Kinetics of Thermal Decomposition of Pentaerythritol tetranitrate Below the Melting Point

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The author derives an equation describing the kinetics of thermal decomposition of organic solids which melt progressively during the reaction. Specifically, he treats the case where the solid responsible for the melting is unstable. The equation is

$$V = K(e^{\lambda t} - \lambda t - 1),$$

where V = the volume of gaseous products at time t, and λ and K are kinetic constants incorporating the reaction rate constants. In the vicinity of the m.p. of the starting reagent, the thermal decomposition of pentaerythritoltetranitrate is satisfactorily described by this equation.

Selection of Catalysts for Homogeneous-Phase Hydrogenation

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The authors have investigated the ability of ions of 62 metals to catalyze the oxidation of molecular hydrogen in 70°C aqueous solutions. Ions of elements of groups IA and IB and of platinum metals are capable of homogeneous activation of H_2. Complexed compounds of platinoid elements and of Cu(II) catalyze the reduction of $Cr_2O_7^{2-}$. Noncatalytic oxidation of H_2 takes place in solutions of compounds whose redox potential is higher than +1.4 volts. The author proves that high-activity catalysts for the hydrogenation must be sought among the coordination compounds exhibiting a metal-metal bond.

Oxidation of *n*-Butenes and Methylacetylene on Mild Catalysts. Studies Involving Differential Calorimetry

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Differential calorimetry was used to study the oxidation of a mixture of *n*-butenes and methylacetylene on a copper and a bismuth-molybdenum catalyst. The catalysis on copper is heterogeneous-homogeneous, while that on bismuth-molybdenum is heterogeneous. It is hypothesized that the mechanism depends on the energies of the bonds between intermediate radicals formed during the reaction and the catalyst surface, as well as on the nature of these intermediate radicals.

Dehydrogenation of Butane in a Circulating System. 1. Kinetics of Butylene Formation and Carbon Deposition

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Dehydrogenation of butane was studied by the circulation technique in a fluid bed apparatus where the catalyst activity was constant. Initially, the activity of the regenerated catalyst increases, only to fall as a result of carbon deposition. The period during which maximum activity can be maintained depends on the temperature and the space velocity of the butane. It is thought that carbon deposition is a process which parallels the main dehydrogenation reaction.

Inversion of *l*-Menthone over a Silica-Alumina Catalyst

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The authors studied the inversion of *l*-menthone to *d*-isomenthone over a silica-alumina catalyst at atmospheric pressure and 180°-360°C. The studies were done in a flow system, with the space velocity varying from 21 to 144 $\min^{-1}$. It was found that at 278°C the degree of conversion of the *l*-menthone over this catalyst does not exceed that previously obtained with a copper catalyst. This phenomenon is apparently due to the protonization of the hydrogen on the copper surface.

K-Spectra of X-Ray Absorption and the Reactivity of Chelate Copper Compounds

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The authors have studied the fine structure of *K*-spectra for X-ray absorption by copper. The copper was in the form of chelate compounds such as 2(O,O) Cu, 2(N,N) Cu, 2(N,O) Cu, 2 (N,S)Cu, as well as in various groups incorporated in the backbones of different monomers and polymers. The authors attempted to evaluate the degree to which ions are involved in the metal-ligand bond within the chelate moiety of various compounds. They also attempted to quantitatively characterize the effect that various groups, which are in the molecule but are not directly linked to the chelate moiety, have on the ionization of this bond. The authors found a correlation between the reactivity of polychelates and the magnitude of the effective charge concentrated on the copper atom. The reactivity of the polymers decreases with the decrease of the effective charge on the copper and with the increase of