JOURNAL OF CATALYSIS 9, 197-205 (1967)

Abstracts of Articles in the Russian Journal, *Kinetics and Catalysis*, Vol. 8, No. 1, 1967. Published by the Siberian Division of the Academy of Sciences of USSR

Use of an Ion Source with an Inhomogeneous Electric Field for Studying Processes Induced by Collisions of Electrons and Ions with Molecules

G. B. Karachevtsev and V. L. Tal'rose

Institute of Chemical Physics, Academy of Sciences, USSR

The authors report mass-spectroscopic data on species obtained by electron impact in an ion source which contains a strong electric field, created around a thin metal filament. About half of the $C_7H_7^+$ fragments produced during ionization of toluene have formation times greater than 10^{-9} sec, but most of the decay processes terminate in less than 2.5×10^{-7} sec. The same filament-containing source was used as an ion trap to increase the dwell time of primary ions in the ion source; in studies of elementary processes, this technique offers several advantages over the conventional ion sources. The rate constants for the reactions $H_2^+ + H_2 = H_3^+ + H$ and $N^+ + O_2 = NO^+ + O$, obtained by the above technique, agree with those obtained by other methods. In addition, some data indicating a reaction of propane-derived ions with krypton have been obtained.

High-Temperature Reactions of Fluoromethanes. 1. Pyrolysis of Methyl Fluoride

S. F. Politanskiy and V. U. Shevchuk

The kinetics of high-temperature decomposition of methyl fluoride were studied at 850°-1100°C in a flow apparatus. The rate constant of this first-order homogeneous reaction is

$$K = 7.41 \times 10^{13} \exp -(82{,}600/RT)\ \mathrm{sec}^{-1}$$

The products consist of hydrogen fluoride, ethylene and products of decomposition of ethylene, that is, hydrogen, methane, acetylene, and coke. These data, as well as thermochemical considerations, indicate that the first step of this reaction is splitting of CH_3F into the diradical CH_2 and HF.

Reactions of α-Oxides. XI. Kinetics of Reactions of Ethylene Oxide with Alcohols in the Presence of Boron Fluoride or Metal Halide Catalysts

V. M. Kozlov and N. N. Lebedev

The Mendeleyev Chemical Engineering Institute, Moscow

The reactions of ethylene oxide with methyl and octyl alcohols in the presence of BF_3 proved to be first order with respect to EtO and BF_3 while exhibiting a complex dependence on the alcohol concentration. The activity of various catalyst employed can be ordered as follows: $BF_3 > SbCl_5 > SnCl_4 > FeCl_3 > TiCl_4$. In solvents with low dielectric constants, protonated acids are less active than BF_3, but are more active in strongly dissociating media.

Activity of Catalysts in Concerted Polymerization

G. A. Baranova, L. L. Stotskaya, and B. A. Krentsel'

The Topchiev Institute of Petrochemistry, Academy of Sciences, USSR

The authors discuss the possibility of creating catalysts for the homogeneous polymerization of vinyl monomers. Comparison of homogeneous and heterogeneous catalysts would seem to indicate that no major mechanistic changes should result from the replacement of one catalyst by the other. During the stereospecific polymerization in the presence of a complexed metalorganic catalyst, the controlling factor is the compound formed by the transition metal. The latter will participate in the formation of an active site regardless of whether the catalyst as a whole is in the same or in another 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

YU. M. SIVERGIN, G. I. LIKHTENSHTEYN, AND A. A. BERLIN
Institute of Chemical Physics, Academy of Sciences, USSR

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

YU. L. SPIRIN
Institute of High Polymer Chemistry, Academy of Sciences, Ukr. SSR

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

KH. S. BAGDASARYAN AND E. A. TROSMAN
The Karpov Physicochemical Institute

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

N. V. YABLOKOVA, V. A. YABLOKOV, AND A. V. BADYANOVA
The Lobachevsky State University, Gorkiy

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.

R. P. TIGER AND S. G. ENTELIS
Institute of Chemical Physics, Academy of Sciences, USSR

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

B. I. KAYDYMOV
The Clement of Ochrida University, Sofia, Bulgaria

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