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A Theory of Low Temperature Interaction of Atomic Hydrogen Formed in Gaseous Phase with Solid Olefins

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Interaction of atomic hydrogen, which is produced in gaseous phase, with solid olefins was determined by formal analytical methods. Individual partial reaction mechanisms were also investigated. Equations were derived to correlate rate constants, k_1 and k_2, of the reactions, $Ol + H\cdot \xrightarrow{k_1} R\cdot$ and $H\cdot + H\cdot \xrightarrow{k_2} H_2$, with the atomic hydrogen coefficients of diffusion in the hydrocarbons studied. These correlations were based on the experimental data of the effect of thickness of the paraffinic layers formed over the olefins upon their hydrogenation rates.

Radiative Oxidation of Heptene-1

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A study of radiative oxidation of heptene-1 with molecular oxygen shows that initial formation of peroxide and carbonyl compounds via a chain mechanism occurs at a low temperature of 8°. The effective activation energy of formation of these products from heptene-1 is lower than from *n*-heptane (3.8 ± 0.5, for $C_7^{=} - 1$; 6.0 ± 1.0 kcal/mol, for n-C_7). Radiative oxidation of *n*-heptane-heptene-1 mixtures results in appreciable increase of oxidized product yields, the greatest sensitizing action occurring at heptene-1 concentrations under 10 mole per cent. The sensitizing effect is associated with the transfer of energy from *n*-heptane to heptene-1.

Air Oxidation of Uranium Dioxide in Presence of Added Carbonates and Oxides

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This study shows that added alkali metal carbonates and the oxides: ThO_2, ZrO_2, TiO_2, U_3O_8, exert appreciable effect upon the rates of UO_2 oxidation with air at various stages of the process. These stages are marked by significant changes in crystalline structure of the oxidate. Some of these additives facilitate the formation and growth of new phases; others, on the contrary, prevent their occurrence by forming chemical compounds with the nuclei of new phases.

These additives are also effective when oxidation of UO_2 is carried out with limited amounts of adsorbable oxygen.

A Mechanism of Thermal Stabilization of Silver Oxalate by Addition of Cadmium Ions

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Addition of cadmium ions in concentrations of 0.1–0.5 mole % decreases conductivity of ionized $Ag_2C_2O_4$, whereas additions of this ion in amounts of 1.5–10 mole % has the opposite effect on conductive properties of this salt. A discussion of probable reasons for this effect includes possible recombination of the interstitial Ag^+ cations with the cationic vacancies. The character of the reflection and adsorption spectra in the visible and ultra-violet regions is not altered by the additive.

The rate of thermal decomposition of $Ag_2C_2O_4$ decreases on addition of ionic cadmium in the amounts stated. The observed decrease of the rate is regarded as a consequence of the effect of changes in the concentration of the cationic vacancies upon the elementary thermal decomposition stages of the process.

Formation of Radicals in Low Temperature Radiolysis of Toluene

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The EPR spectra of the radicals formed in irradiation of frozen $C_6H_5CH_3$ and $C_6D_5CH_3$ by high velocity electrons were compared with the EPR spectra of phenyl, benzyl and cyclohexadiene radicals obtained in earlier studies. The comparative data show that the hydrogen atoms which are split off in the initial reaction step from the CH_3 group and from the phenyl ring have different reactivities. Basically, the hydrogen atoms from phenyl groups enter into addition reactions, forming radicals of cyclohexadiene-type; whereas those from the CH_3 group—due to their greater kinetic energy content—are primarily consumed in the secondary reactions of atomic hydrogen split-off from toluene molecules.

Kinetics of Heterogeneous Catalytic Reactions in Chromatographic Pulsed Flow Units at Conditions of Ideal Linear Chromatography

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The authors analyze from a theoretical standpoint the kinetics of heterogeneous catalytic reactions of different orders. The reactions are assumed to be carried out in pulsed flow units at the conditions of ideal linear chromatography. The equations derived to evaluate the rate constants and activation energies of the first order reactions are used in processing the experimental data on dehydrogenation of cyclohexane to benzene over a number of catalysts. The effect of various types of pulsed feed on conversion is also shown.

Kinetics of Liquid Phase Hydrochlorination of Acetylene in Presence of Cuprous Chloride

By R. M. Fleed, N. F. Alekseiyeva, T. G. Khmelevskaya, and N. A. Gaidai

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The kinetics of hydrochlorination of acetylene in liquid phase at 40°–98° was studied, using $CuCl—MeCl—HCl—H_2O$ and $CuCl—HCl—H_2O$ as the contact solvents. The reaction rate constants bear linear relationship to activity of the catalyzing ions. The conditions to select contact solvents of optimum composition are described.

Chemiluminescence in Slow Chemical Reactions: Investigation of Kinetics of Accumulation of Hydroperoxide in Catalytic Oxidation of Ethyl Benzene by a Chemiluminescence Technique

By I. V. Zakharov and V. Ya. Shliapeentokh

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This study of the chemiluminescence-controlling factors during initial stages of oxidation of ethyl benzene in a catalytic solution of cobalt acetate in glacial acetic acid shows that the change in chemiluminescence intensity with reaction time is directly tied to the kinetics of hydroperoxide accumulation. A chemiluminescence technique is proposed to determine the hydroperoxide decomposition rate constants in the course of the oxidation process. The rates of oxidation and concentrations of hydroperoxide at steady state conditions were also determined by use of this technique.

Mechanism and Kinetic Principles of Dimerization of 1,1-Diphenylethylene in Aqueous Sulfuric Acid

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A spectrographic study of kinetics of dimerization of 1,1-diphenylethylene in aqueous (64–68%) sulfuric acid was carried out at temperatures of 5°, 20° and 40°. In terms of decreasing carbonium ion concentration, the rate of the second order reaction decreases with increasing concentration of the acid. At the conditions studied, the reaction temperature has practically no effect upon the rate.

To explain observed regularities of the process, production of the dimer is assumed to occur by two parallel routes: (1) interaction of 1,1-diphenylethylene with carbonium ions and (2) interaction of carbonium ions with diphenylmethylcarbinol, which is produced from the olefin in presence of aqueous sulfuric acid. The values of activation energies and reaction rate constants for the two processes are listed.

The conclusions presented satisfactorily agree with the earlier-published (1) principles of ionization of 1,1-diphenylethylene.

Liquid Phase Dehydrogenation of Isopropyl Alcohol

By S. L. Keeperman, N. V. Neekolayeva and I. P. Davidova

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A study of the mechanism and kinetics of liquid phase dehydrogenation of isopropyl alcohol was carried out over a skeletal nickel catalyst. The reaction which in the initial stage is of zero order, approaches a near-zero order at the subsequent steady state conditions—although at a much slower rate.

The data on reaction kinetics, catalytic ac-