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Oxidation-Reduction Transformations of Acceptors in Organic Solvents Induced by Ionizing Radiation: Reduction of Permanganate Ions in Acetone Solutions

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A study was made of the radiation-induced reactions of permanganate ions dissolved in acetone. Irradiation reduces the permanganate ions to form manganese dioxide. The yields of the dioxide increase with the ion concentration, reaching 23 equivalents/100 ev in a 0.002 M solution. A post-radiative reduction of permanganate was uncovered, the product yields decreasing with increasing concentrations of the permanganate. The over-all reduction yields increase with increasing concentrations of permanganate. For the 0.002 M solutions, the over-all yield is about 42 equivalents/100 ev. A possible permanganate ion reduction mechanism is discussed as resulting from interaction of the ions with the products of acetone radiolysis.

Desoxybenzoin, a Molecular Intermediate in Oxidation of 1,2-Diphenyl Ethane with Potassium Permanganate

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Oxidation of 1,2-diphenyl ethane by aqueous solutions of potassium permanganate was studied at temperatures of 56°–90°. Properties of desoxybenzoin, an intermediate product of this reaction, were also determined. It was found that desoxybenzoin oxidizes to the same products as the diphenyl ethane: dibenzoyl benzoic acid and CO_2—but that it does so at a much faster rate. In oxidation of 1,2-diphenyl ethane, the rates of formation of desoxybenzoin and of dibenzoyl are of the same order of magnitude. Consequently, desoxybenzoin is the principal intermediate product in the diketone formation. A mechanism of oxidation of 1,2-diphenyl ethane is described.

Radiative Oxidation of Two-Phase Hydrocarbon-Water Systems

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The experimental results of radiative oxidation of two two-phase hydrocarbon systems, n-heptane-water and n-heptene-water, show that with small radiation dosages the yields of peroxides, carbonyls, acids, and alcohols equal to the combined yields of products of radiolysis of individual phases of each system. In one-step processing of the two-phase systems, this fact is obscured as a result of the product redistribution between the phases by the irradiation-induced mixing.

The yields of the acids from aqueous solutions of heptene-1 exceed those from radiative oxidation with oxygen of pure heptene-1.

Oxygen-Initiated Heterogeneous Catalytic Condensation of Olefins in Presence of Hydrogen: Conversion of Propylene

By N. I. Yershov, Ya. T. Eidoos, V. R. Yerokheena, and N. S. Andreiyev

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Like ethylene, at suitable conditions propylene condenses to form liquid products. In presence of hydrogen and small amounts (1-2%) of oxygen, the product yields over a cobalt-clay catalyst at 100° are about 35% of the C_3H_6 charged. In addition to the C_6 and C_9 polymers, the reaction products contain molecules of hydrocarbons with carbon numbers not divisible by 3: such as C_4, C_5, C_7, C_8, etc. The polymerization reaction is initiated by small amounts of oxygen and, apparently, belongs to the chain-radical class of reactions.

High-Dosage Radiolysis of Neutral Solutions of Nitrate Salts

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Radiolysis of neutral aqueous solutions of $NaNO_3$ was investigated at various solution concentrations and x-ray dosage rates. The NO_2^- ion yields were determined by irradiation of solutions containing nitrite and hydrogen peroxide. With dilute- and medium-strength solutions, increasing the x-ray dosage rates also increases the values of $G(NO_2^-)$ and $G(H_2O_2)$. For 1 M solutions of $NaNO_3$, the values of $G(NO_2^-)$ are independent of the dosage rates. A mechanism is proposed to explain the radiolytic reduction of the nitrate ions. The distinguishing feature of the postulated mechanism is competition between the reverse oxidation of the NO_2^- ions by the OH radicals and the recombination of the radicals.

In irradiation of relatively dilute $NaNO_3$ solutions by powerful pulsed beams, recombination of the hydrogen atoms, originating from various tracks, plays an important role.

Determination of Absolute Rate Constants of Free Radical Reactions: Addition of Trichloro-Bromo-Methane to Cyclohexane and to Heptene-1

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A new method is proposed to investigate the non-stationery kinetics of chain reactions. This method involves measuring the non-adiabatic temperature rise following complete or partial cessation of the photochemical initiation. Using this method, the following rate constants (as l/mol × sec) were obtained: $CCl_3^{\cdot}$ + cyclohexane, 773 (at 25°); $CCl_3^{\cdot}$ + Heptene-1, $2.30 \times 10^9 \exp(-7000/RT)$; $C_7H_{14}CCl_3^{\cdot} + CCl_3Br$, $2.48 \times 10^9 \exp(-8500/RT)$; $CCl_3^{\cdot} + CCl_3^{\cdot}$, 1×10^8; $C_7H_{14}CCl_3^{\cdot} + C_7H_{14}CCl_3^{\cdot}$, 1.0×10^6. A comparison with published data shows that the constants of addition of $CH_3^{\cdot}$ and $CCl_3^{\cdot}$ radicals to cyclohexene, heptene, vinyl acetate, anthracene, and styrene increase in the order mentioned. The absolute values of the constants for these radicals differ but little.

Synthetic Zeolites as Ion Exchangers: Study of Kinetics of Ionic Exchange

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The results of a study of kinetics of ionic exchange processes are summarized for various systems of synthetic zeolites and solutions of LiCl, NH_4Cl, NH_4NO_3, $CaCl_2$, $MgCl_2$, and $PC(NO_3)_2$. For the solution concentrations of 0.1 to 1.0 N, external diffusion processes control the ion exchange rates. Agglomeration of the original particles into larger aggregates does not substantially decrease the exchange rates.

Effect of Reaction Temperatures on the Rates of Addition of Atomic Hydrogen to Some Solid Unsaturated Hydrocarbons

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A method is described to measure the rates of consumption of atomic hydrogen (being produced in the gaseous phase) by certain solid unsaturated hydrocarbons. For the adsorbed-hydrogen layers at 63° to 160°K, the adsorption rates are temperature-dependent. Effective activation energies were determined in hydrogenation of a number of unsaturated hydrocarbons. For some of these compounds, the relatively minor differences in the heterogeneous hydrogenation rates are accompanied by significant differences in the effective activation energy values.

Effect of Additives and Conditions of Preparation of Zinc Oxide on Its Performance in Isotopic Oxygen Exchange Reactions

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A study was made of the effects of Li, Ga, and In additives in ZnO catalyst and of the catalyst preparation conditions upon the kinetics of isotopic oxygen exchange. Increasing calcination temperature of pure ZnO from 850° to 1200°, increases the exchange rate to some extent. Li added to ZnO in amounts of 0.5–0.75 atom % at 850° increases the rate of isotopic oxygen exchange with the ZnO catalyst so that it exceeds