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Liquid and Gaseous Phase Oxidation of Methyl-Ethyl Ketone

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The changes in the kinetics and the product compositions when going from liquid to gaseous phase oxidation of methyl-ethyl ketone are caused not only by changes in reactant concentration but also by the change in the polarity of the medium.

MEK is consumed by a chain reaction only, whereas its oxidation products, diacetyl and keto-hydro peroxide, are consumed via a chain and a non-chain reaction processes. One non-chain decomposition path leads to formation of the radicals by degenerative chain branching. Aside from the chain reaction path, acetic acid is also formed by the non-chain conversion of diacetyl to two molecules of the acid.

The chain branching processes of MEK oxidation are the same in the liquid and the gaseous phase.

Alkylation of Chlorobenzene with Isopropyl Chloride in Presence of Aluminum Chloride

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The kinetics of alkylation of chlorobenzene with isopropyl chloride in presence of aluminum chloride was studied at temperatures of 0°, 20°, and 60°, and kinetic equations for the reaction system developed at various molar ratios of isopropyl chloride to chlorobenzene. The results show the effect of the molal ratios of these reactants on yields of isopropyl chlorobenzene.

A Study of Kinetics of Isotopic Exchange Between Gaseous Oxygen and the Oxygen in Complex Organic Compounds of Cobalt

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Isotopic exchange between gaseous oxygen and the oxygen in the complex organic compounds of cobalt, bis-(N,N'-disalicylal-ethylenediamine)- μ -

aquodicycobalt and bis-[N,N'-di-(3-nitrosalicylal)-ethylenediamine]- μ -aquodicycobalt, was studied.

The isotopic exchange rates are a complex function of the reaction temperature. A mechanism is offered to explain the rate-temperature relationship.

Effects of Temperature and Irradiation Dosage Upon Radiolysis and Oxidation of Diisopropyl Ether

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X-ray irradiation of diisopropyl ether was studied. In absence of oxygen, the radiolysis results in formation of alcohols by a non-chain mechanism and in simultaneous production of aldehydes via a chain reaction mechanism. The activation energy of the latter reaction is 11 kcal/mole.

In presence of oxygen, the irradiation at low temperatures results in a non-chain type formation of peroxides and carbonyl compounds. Reaction temperatures of 10°, and higher, result in chain reactions with activation energies of 15 to 20 kcal/mole, the value increasing with temperature.

Basic Reaction Rate Constants for Oxidation of Ethylbenzene by Molecular Oxygen

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In intermittent oxidation of ethylbenzene by elementary oxygen the reaction rate constants were determined for the reactions involving continuous and interrupted chain formation. Also determined were the rate constants for the peroxy radical of ethylbenzene inhibited with α -naphthol and β -naphthol.

Kinetics of Oxidation of Hydrazine by Aqueous Solution of Nitric Acid

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The kinetics of oxidation of hydrazine by

aqueous solutions of HNO_3 in concentrations of 2.2 to 8.2 moles/L was studied. The reaction was first order relative to hydrazine, and third order relative to acid. At 97° the reaction rate constant is $(2.7 \pm 0.2) (10^{-5}) \text{ mole}^{-2}\text{L}^3\text{min}^{-1}$ and the activation energy is $27.2 \pm 0.8 \text{ kcal/mole}$. Also established were the stoichiometry for the process and the composition of the reaction products.

A possible reaction mechanism is proposed which assumes the formation as intermediates of nitrous acid, tetrazine, isotetrazine, etc. The reaction between N_2H_4 and NO_2 is the rate limiting step.

Reduction of Uranium Trioxide by Ammonia

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The kinetics of reduction of uranium trioxide by ammonia was studied at temperatures of 300° to 425° and reducing gas pressures of 10 to 600 mm Hg. An equation correlating the rate to pressure is proposed. An apparent activation energy was determined. A mechanism is proposed, and desorption of molecular nitrogen from the oxide surface shown to be rate limiting.

Effect of Pre-Irradiation on the Subsequent Thermal Decomposition of Permanganates of Metals of the First Group in the Periodic Table

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The effect of 200 keV X-ray exposure upon subsequent thermal decomposition rates of permanganates of lithium, potassium, rubidium, cesium, and silver was studied. Irradiation increases thermal decomposition rates of the various permanganates in the order in which they are listed.

The results disagree with Prout's Theory, according to which the acceleration of thermal decomposition is due to production of dislocations. The theory is critically re-examined in the light of the new experimental data. It is proposed that the observed increase in thermal decomposition of the irradiated samples is caused by the catalytic action of radiolysis products observed in the lattice of the solids.

The overall product yields are proportional to the amount of products formed in the irradiation step. The yield depends on free volume, ionization potential of the cation, and the polarizing interaction between the cation and the permanganate anion.

Reaction Kinetics Including Participation of the Solid Phase: Kinetic Equations and Determination of Specific Reaction Rates

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The kinetics of heterogeneous catalytic reactions were examined to establish empirical laws for the formation and behavior of the intermediate product complexes ("the nucleous stage of product formation"). Kinetic equations convenient for treatment of experimental data are presented. A unified method is proposed to determine specific rates of heterogeneous catalytic reactions with different kinetic mechanisms suitable for comparing reactivities of various substances.

Experimental data for the oxidation of an iron catalyst by water in a carbon monoxide-hydrogen synthesis process are used as an example.

A Theory of Chemisorption on Polar Crystals

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The adsorptive properties of ionic crystals are determined by the nature of chemical bonding, i.e., by the degree of ionic and homeopolar bonding. Since electrical properties of crystals are also related to the nature of their chemical bonds, a correlation exists between the electrical and the chemisorptive properties of crystals.

Surface defects of crystals change the nature of the neighboring chemical bonds. Thus conditions arise which either favor or hinder chemisorption and modify catalytic activity.

Soluble Complexes of Unsaturated Hydrocarbons and Metallic Salts and Their Role in Catalytic Reactions: Soluble Compounds of Acetylene and Silver Salts

By O. N. TIOMKEEN, R. M. FLEED,
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The thermodynamics of the system acetylene with silver sulfate in H_2SO_4 was studied with the aid of potentiometric technique, over wide ranges of temperatures and concentrations, with respect to formation of the π -complex, AgC_2H_2^+ , and of asymmetric acetylenide, AgC_2H . The poor catalytic activity of silver salts for hydration of acetylene, as compared to that of copper salts, is explained by the relatively small value of the equilibrium constant for formation of the silver-acetylene π -complex.