JOURNAL OF CATALYSIS 2, 254–257 (1963)

Kinetics and Catalysis, Vol. IV, Issue 1, pages 24–34 (Jan.–Feb. 1963)

Free Radical Recombination Processes on Semi-Conductor Surfaces and Their Role in Luminescence

By F. F. Volkenshtein, A. N. Gorban, and V. A. Sokolov

Tomsk Polytechnical Institute, Institute of Physical Chemistry of the Academy of Sciences of U.S.S.R.

The mechanism of luminescence in luminofors was studied as possibly occurring by the radical recombination route under the influence of chemically active gases and by "cando"-luminescence. The intensity of the radical-recombination luminescence was calculated in terms of pressure and the levels of Fermi state. The effect of an outside electric field on the intensity of "cando"-luminescence was determined experimentally. The results qualitatively agree with the theory proposed.

Possible Explanation of the Compensating Effect in Some Chemical Reactions

By G. E. Leehtenshtein

The Institute of Chemical Physics of the Academy of Sciences of U.S.S.R.

The compensating effect can be rationalized by assuming that (1) the experimentally-determined effective rate of a reaction studied is the sum of the local rates which are independent of each other and (2) the free activation energies follow the Gaussian frequency distribution.

Decomposition of Molecular Ions Formed in Photoionization of Hydrazine and of Some of Its Alkyl Derivatives

By M. E. Akopyan and F. I. Veelesov

Institute of Physics of the Leningrad State University

Summarizes the results of studies of the mass spectra and of the ion formation potentials in photoionization of hydrazine; methyl hydrazine; 1,1-dimethyl hydrazine; and 1-methyl 1-normal butyl hydrazine. Gives calculated values of heats of formation of the ions, ionization potentials of the radicals, and dissociation energies of some of the bonds.

Formation of Free Radicals in the RH + O_2 System: I. Tetralin, Cyclohexanol, Cyclohexanone

By E. T. Dieneesov

The Institute of Chemical Physics of the Academy of Sciences of U.S.S.R.

The mechanism of free radical formation (chain initiation) in an $RH + O_2$ liquid phase system was studied by use of an inhibition technique. Based on the results for tetralin and cyclohexanol, show that the radicals are formed according to the reaction, $2RH + O_2 \rightarrow 2R\cdot + H_2O_2$. List values of the reaction rate constants for tetralin, cyclohexanol and cyclohexanone.

Determination of Absolute Rates of Chain Initiation and Growth in Anionic Polymerization of Styrene

By H. S. Bagdasaryan and N. I. Niepomnyashchii

The L. Ya. Karpov Physico-Chemical Institute

The kinetics of chain growth was studied in a single-pass continuous unit by reacting the "live" polymers of styrene with the monomer in a tetrahydrofuran solution. The chain growth rate constant is $k_p = (1.00 \times 10^6)\cdot\exp(-4{,}670/RT)$ l/mol-sec.

An analysis of the kinetic data for interaction of sodium diphenyl with styrene shows that conversion of the ion-radicals of styrene into the dianionic dimers is the limiting step in the "live" polymer formation process. The rate constant for this reaction is $k_2 = (5.6 \times 10^{11})\cdot\exp(-14200/RT)$ l/mol-sec. The effects of solvation and interaction of the ions upon the activation energies and entropies of the reactions studied were also examined.

Mechanisms of Energy Transfer in Luminescence and Chemical Radiation

By V. A. Krongauz and I. N. Vaseeliyev

The L. Ya. Karpov Physico-Chemical Institute

Radiolysis and luminescence of three component solutions: toluene, benzoyl peroxide, and a luminophor (e.g., n-terphenyl or 2,5-diphenyl axazole) were studied. The protective action of luminophors against the radiation-sensitized decomposition of the peroxide and extinguishing by the peroxide of the photo- and radio-luminescence of luminophors can be explained by hypothesizing the existence of a competing transfer of energy from the solvent to the two acceptors and from a luminophor to the peroxide. The energy transfer from toluene to benzoyl peroxide and to luminophors occurs by a "remote-action" mechanism although displacement of the interacting molecules by diffusion also exerts substantial effect. The transfer of energy from a luminophor to the peroxide apparently occurs by a diffusion mechanism, via the formation of an intermediate complex from the peroxide and the excited molecules of a luminophor.

Reduction of Uranium Trioxide by Mixtures of Nitrogen and Hydrogen

By V. G. VLASOV AND V. M. JOOKOVSKII

S. M. Keerov Polytechnic Institute in the Urals

Kinetics of reduction of uranium trioxide by hydrogen-nitrogen mixtures was investigated at temperatures of 350°–500° and pressures of 25–600 mm. Hg. Apparent activation energy of this reaction was found to be 26.5–31.7 kcals/mole. Show comparative characteristic data for reduction of uranium trioxide by pure hydrogen and ammonia.

Comparative Kinetic Properties of Kationites KU-1, SDV-3, SM-12 and SBS

By G. M. PANCHENKOV, V. I. GORSHKOV, AND V. I. SLOVETZKII

Chemistry Department of the M. V. Lomonosov State University in Moskow

The kinetics of ion exchange was studied by contacting 0.01–1.0 *N* NaCl solutions at temperatures of 6°–35° with thin layers of H-type cationites: SDV-3, SM-12, KU-1, and SBS.

Catalysis of Solid Phase Reactions: Thermal Decomposition of Ammonium Perchlorate in Presence of Ferric Oxide

By F. SHOLMOSHEE AND L. REVES

The Institute of Inorganic and Analytical Chemistry of the Seged University, Hungary

Catalytic action of ferric oxide upon ammonium perchlorate at various stages of decomposition was investigated at identical operating conditions. At 210°–240° ferric oxide exerts only minor effect upon the reaction rate, but at 245–270°, and at elevated temperatures, its catalytic action is significant. Consideration of the kinetic data leads to the conclusion that ferric oxide accelerates the anion-to-cation electron transfer, the reaction controlling step.

Kinetics of Solid Phase Reactions: II. Hydrogenation of Iron Carbides

By A. YA. ROSOVSKII, A. A. IVANOV, YU. B. KAGAN, AND A. N. BASHKEEROV

The Institute for Petrochemical Synthesis of the Academy of Sciences of U.S.S.R.
The M. V. Lomonosov Institute for Fine Chemical Technology

A study of the kinetics of hydrogenation of the iron carbide formed in an iron catalyst for synthesis of CO and H_2 shows that the kinetic concepts developed earlier also apply to this reaction. The specific reaction rates and activation energies were determined using pertinent calculation methods employed in the earlier study. The value of the activation energy so obtained agrees with that determined independently from a reaction rate-temperature correlation at various fixed conversion values.

Correlation of Catalytic Activity of Semiconductors with the Constants Characterizing Their Photoconductivity and Photoconductivity Kinetics

By V. A. JOORAVLIOV AND V. N. KOOLEETZKII

Physics Department of Lvov Medical Institute

The constants characterizing photoconductivity and kinetics of photoconductivity of semiconductors are correlated with their catalytic activity. This correlation study shows that only the photoconductivity relaxation periods are correlatable with the activity values. Existence of this correlation follows from the electronic theory of catalysis and the assumption that catalytic reactions are preceded by desorption of the adsorbed particles.

Reactions of α-Oxides: II. Kinetics of Reaction of Ethylene Oxide with Acetic and Monochloroacetic Acids

By N. N. LIEBIEDIEV AND K. A. GOOSKOV

D. I. Mendeleyev Chemico-Technological Institute in Moscow

Kinetics of reaction of ethylene oxide with acetic and monochloroacetic acids was studied