is stopped by injection of α-naphthylamine. This fact indicates that these products are formed via a chain mechanism.

Acetophenone is formed in recombination of the peroxide radicals and in decomposition of the oxycumene radicals. Basically, dimethylphenylcarbinol is produced in decomposition of the hydroperoxide. The rate of cumene hydroperoxide decomposition into radicals is not affected by the addition of dimethylphenylcarbinol and acetophenone.

In the presence of benzoic acid, the hydroperoxide decomposition rate, v, is described by the equation:

$$v = k[C_6H_5C(CH_3)_2OHH][C_6H_5COOH].$$

With chlorobenzene as the solvent, the value of k is $7.1 \times 10^6 \exp(-20600/RT)$ liter/mol-sec.

Kinetics of Reaction of Divalent Ions of Iron with Diphenylpicrylhydrazyl

R. I. Zoosman, Yu. I. Nab'yerookheen,
Yu. N. Moleen, and N. V. Voyevodsky
Institute of Chemical Kinetics and Combustion of Siberian Division of the Academy of Sciences of USSR

A spectrophotometric study was made of the general kinetic relationships governing reactions of Fe^{++} ions with diphenylpicrylhydrazyl (DPhPH). In a mixture with a 74% alcohol —26% water solution, the reaction rate is expressed by the equation: $W = kRM$, where R is concentration of the radical and M is concentration of Fe^{++} ions. The reaction products are Fe^{+++} and diphenylpicrylhydrazyl only, which is in agreement with the published data. The effective activation energy and the preexponential factor values are 8.1 ± 0.5 kcal/mol and 1.2×10^8 liter/mol × sec, respectively.

Qualitative data were obtained of the effects of pH of the media and the nature of the solvents and the ligands on the reaction rate.

Interaction of Atomic Oxygen, Produced in the Gas Phase, with Solid Hydrocarbons: Reactions of the Atomic Oxygen with Solid Propylene at Temperatures of 77°–67°K

V. M. Orlov and A. N. Ponamar'yov
Institute of Chemical Physics of the Academy of Sciences of USSR

The effects of the temperature of a solid hydrocarbon and of the degree of atomic oxygen conversion on the reaction rate of the oxygen were determined for the case of solid propylene at 77°–67°K. The results show that the yields of the principal reaction products are: propylene oxide, 54%; propion aldehyde, 43%; and acetone, 3%. The product distribution remains unchanged at the conditions covered in this study.

Alteration by Additives of Physico-Chemical Properties of Solids: Effect of Admixed Heterophase Semiconductors on Thermal Stability of Silver Azide

Yu. A. Zakharov, E. S. Koorochkeen,
G. G. Sav'yel'yev, and Yu. N. Roofov
S. M. Keerov Polytechnical Institute in the City of Tomsk

A study was made of the effect of admixed heterophase semiconductors: CdO, ZnO, NiO, Ni_2O_3, Bi_2O_3, CdS, CoO, Co_2O_3, and Co_3O_4 — on the rate and activation energy of thermal decomposition of AgN_3. In this reaction, catalytic activity of the semiconductors for production of the respective compounds increases with increasing electron work function of the semiconductors at the decomposition conditions employed.

The changes in activity of the semiconductors were determined following the irradiation and partial thermolysis of the AgN_3 — semiconductor mixtures. The effect of the admixed semiconductors on the AgN_3 decomposition rate is compared with the effect of static electric field on the rate of decomposition of "pure" AgN_3. The results obtained are discussed in the light of the concepts advanced by the authors regarding the decisive role played in catalytic thermolysis of solids by the contact phenomena and by the processes on the border of separation of solid-semiconductor mixtures onto the phases.

The nature of the elementary limiting stage of the AgN_3 decomposition process is considered.

Effect of Admixtures on Radiolysis of Potassium Nitrate

V. V. Boldir'yev, V. M. Likheen,
A. N. Obleevantzev, and K. M. Saleekhov
Institute of Chemical Kinetics and Combustion of Siberian Division of the Academy of Sciences of USSR Scientific Research Institute of Nuclear Physics of the Tomsk Polytechnical Institute

The effect of admixtures of Tl^+, Sr^{++}, Pb^{++}, and $SO_4^=$ was determined in radiolysis of potassium nitrate by the γ-rays of Co^{60}. The results show that in the radiation-chemical conversion of KNO_3, the yield of the end product, potassium nitrite, is increased by small dosages of the Sr^{++} and Pb^{++}, whereas in large dosages these additives decrease the KNO_2 yield. In addition, the Tl^+ in the dosages used increases the product yield. The probable reasons are discussed to explain the effects of the additives on the radiolysis process. The authors suggest that the differences in the KNO_2 yields obtained in radiolysis of an identical KNO_3 feedstock might be tied-up with the effect of the impurities in the feedstock.

The Mechanism of Isocyanate Interaction with Alcohols

I. A. Proneena, Yu. L. Speereen,
A. A. Blagonravova, S. M. Ar'yef'yeva,
and A. P. Gantmakher

The State Scientific Research and Planning Institute for Paint Varnish Industry

The effects of temperature and of concentration of the reaction components on the rate of urethane formation were determined dilatometrically. The activation energies of the process were determined, using toluene and tetrahydrofuran as the solvent media. The results show that although the reaction is catalyzed by tertiary amines, tetrahydrofuran in small concentrations is catalytically inactive. In addition, the end product, urethane, also does not catalyze the reaction.

The reaction mechanism proposed includes the reactions of association of the alcohols and of formation of the isocyanate-alcohol complexes in hydrocarbon media and of the isocyanate-solvent complexes in polar media.

Kinetics of Catalyzed Hydrolysis of Allyl Chloride in Alkaline Media

Yu. A. Tr'yeg'yer, R. M. Fleed,
and N. A. Vorontzova

M. V. Lomonosov Institute of Fine Chemical Technology in the City of Moscow

The investigation of kinetics of hydrolysis of allyl chloride was carried out with and without promoting the reaction by different copper catalysts. Based on the overall rate, the process is of the first order with respect to both the allyl chloride and the alkali.

A generalized equation is proposed to describe kinetics of process. The equation takes into account the increasing retardation effect owing to accumulation of the product allyl alcohol due to the non-stationary character of the process. The activation energy and the heat of adsorption were calculated at the reaction conditions of this study. A relationship is shown to exist between the adsorption- and the complex-formation steps. Based on the kinetic data and X-ray analyses of the copper catalyst samples, certain assumptions are made to explain catalytic activity of the metallic copper, which is present as a separate phase in the oxides of copper.

Reactions of α-Oxides: Acid Catalyzed Reactions of Ethylene Oxide with Alcohols and with Other Oxygenated Compounds

N. N. L'yeb'yed'yev and V. M. Kozlov

D. I. M'yend'yel'yeyev Chemico-Technological Institute of the City of Moscow

Two reactions occur in acidic catalysis of ethylene oxide: with respect to the oxide, one of these reactions is of the first order and the other one is of the zero order. Depending on the strength of the acid catalyst, the rate of the first order reaction can be either independent of the alcohol concentration or it can vary linearly with the concentration, increasing or decreasing upon addition of a like ion. The latter reaction comprises an interaction of the protonated oxide with the reagent.

The initial step of the zero order reaction is formation of the glycol ester with the acid catalyst via addition of the acid to the ethylene oxide; in the subsequent step, the ester undergoes alcoholysis. The results show that the addition step is a reaction of the first order relative to both the oxide and the acid; on the other hand, the reactions of oxyethylation and alcoholysis are of the first order with respect to the ester and approximately of the second order with respect to the alcohol.

The Mechanism and Kinetics of Catalyzed Interaction of Isocyanates with Alcohols in the Presence of Organotin Compounds: Reaction Kinetics of *n*-Chlorophenylisocyanate in the Presence of Dibutyldilaurinate of Tin

S. G. Ent'yelees and O. V. N'yest'yerov

Institute of Chemical Physics of the Academy of Sciences of USSR

A spectrophotometric study was made of the reaction kinetics of *n*-chlorophenylisocyanate with methyl alcohol dissolved in *n*-heptane, in the presence of dibutyldilaurinate of tin. At the temperatures and concentrations of the reactants employed, the experimentally-determined rates show that the reaction is of the first order with respect to both the isocyanate and the catalyst. Formation of a complex between the catalyst and the alcohol was uncovered. The value of the equilibrium constant was determined spectrophotometrically and the values of ΔH and ΔS of the complex-formation were calculated.