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Mass Spectrometric Determination of the Rate Constants of Elementary Chemical Reactions: The Theory and Method of the "Diffusion Cloud" Technique in Continuous Flow Systems

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A method is described to study elementary reactions in the gaseous phase with participation of the atoms and radicals. The method involves a mass-spectrometric determination of concentration of the reactants in the mixtures produced by diffusion-mixing in continuous-flow systems. A method to calculate the reaction rate constants is described for a series of reactions, such as:

$$A + B \rightarrow C +$$
$$A + C \rightarrow D +$$

when reactant A is present in appreciable excess.

The changes in the character of the reactions in the gas phase and in concentrations of the reaction components were evaluated in terms of the effects of the reactor walls and of the cone-shaped opening to admit the product stream into the mass-spectrometer. Criteria are listed for selection of operating parameters which would minimize the above effects in the experimental runs.

Influence of Properties of the Glowing Discharge Products and of the Nature of Their Action-Mechanism on Velocity of the Hydrogen–Oxygen Flames in "Peninsular" Ignition

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A study was made of the effect of different action mechanisms of the unstable discharge products in glowing state on the normal propagation rate of a hydrogen-oxygen flame. To this end, the experimentally-determined rate data were compared with the corresponding kinetic data, which were calculated with the aid of electronic computers. The effect of the oxygen in atomic state is not great. The accelerating effect by the glowing discharge products is attributed to the oxygen in excited state which produces rapid branching of the combustion process.

Effect of Solvents on the Elementary Chain-Continuation and Chain-Interruption Reactions in Oxidation of Methylethylketone

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The ratio of the rate constant, k_2, of a continuing chain reaction, to the square route of the rate constant, k_6, of the chain-interrupting reaction was determined in oxidation of methylethylketone in various solvents at temperatures of 40°–70°. The magnitude of the $k_2/\sqrt{k_6}$ ratio increases with increasing concentration of the non-polar solvents: C_6H_6, $C_{10}H_{22}$, p-$C_6H_4Cl_2$, and C_6H_5Cl. This finding and the finding that at the above conditions activation energy, E_2, of a continuing chain reaction also increases, demonstrate that the values of k_2 and k_6 decrease with decreasing values of the dielectric constant, ϵ, of the solvents used. With the solvents: CH_3CN, H_2O, C_2H_5OH, and $C_6H_5NO_2$, whose values of ϵ are greater than that of methylethylketone, the value of the $k_2/\sqrt{k_6}$ passes through the minimum as the solvent concentration is increased. Here, the values of k_2 and k_6 are affected not only by magnitude of the ϵ but, also, by other specific properties of the individual solvents.

Investigation of the Mechanism of Cumene Oxidation in the Liquid Phase by an Inhibition Technique: Formation of the Reaction Products and Their Effect on Decomposition of the Hydroperoxide onto Radicals

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In air-oxidation of cumene, accumulation of the hydroperoxide and ketone reaction products 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

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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

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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

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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

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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