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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