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Equilibrium of Isobutylene and Hydrogen Chloride Reaction with Tert-Butyl Chloride Over Nickel Films

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Tert-butyl chloride is readily formed by interaction of isobutylene and hydrogen chloride over nickel films at temperatures of −35° to 12°C. The activation energy of this process is 4 kcal/mol. In absence of isobutyl chloride by-product, the reaction obeys Markovneekov's Rule. The experimental results covering the reaction kinetics are discussed.

Unlike Pt and Pd, Ni—and Fe, too—are weak hydrogenolysis catalysts in the conversion of tert-butyl chloride to isobutane and hydrogen chloride. This is believed to be due to the strong adsorption of chlorine-containing substances by nickel and iron.

Generation of Coherent Induced Radiation in Chemical Reactions

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This generalized discussion covers from the kinetics standpoint the conditions to effect self-excitation in a hypothesized chemical gas generator of quantum radiation. The conditions to realize the basic reaction steps in the subject generator are reviewed. In this case, as well as in many others, a multi-level reaction scheme is the best one. However, the inversion to the basic state can also be achieved via a transitory working-stage conversion of the reaction intermediates, either the free radicals or free atoms. The absolute chemical reaction rates to effect the auto-excitation were determined. In the generators utilizing excited atoms, the required rate of reaction is not great. Depending on the assumptions, the reaction time is of the order of 10^2 to 10^4 sec. Induction of the radiation by means of diatomic or polyatomic particles increases the reaction rate requirements 3- or 4-fold. In these cases, every effort should be made to utilize chain reactions to the utmost. A formal description is given of the kinetic properties of a system of simultaneously occurring chain reactions of the chemical and the induced radiation types. The name of QUANTOCHEMICAL CHAIN REACTION is suggested for combined reactions of this type. The estimated ranges of efficiency and power output for the hypothesized quantochemical generator are 10^{-2} to 10^{-3} and 10^{-2} to 10^2 watts, respectively.

Limiting Conditions in a Theory of Chain Reactions

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In this theory of gaseous-phase chain reactions, an exact determination method is given for the limiting conditions to avoid chain breakage at the reactor walls. These conditions apply to the reactions at a solid-gas interphase, in adsorption of gases, etc. To determine the limiting conditions, distribution of the active centers in terms of the rates near the chain-breaking reactor walls must be determined first of all. For the case at hand, solving Boltzmann's equation gives the answer. The method developed by Gross, Jackson and Ziring gives the required solutions as the zero- and first-order reaction approximations. The zero-order approximation agrees with Sem'yonov's value of the limiting condition. The calculation, assuming the reaction to be of first-order, results only in a minor correction of the zero-order answer. Thus, Sem'yonov's value of the limiting condition is sufficiently accurate for all possible conditions of destruction of the active centers by collision with the reactor walls. Determination of chain reaction limiting conditions by assuming that diffusion controls, is shown to be valid even at relatively low pressures. A new method is described to determine the limits of applicability of the diffusion-controlling stage.

Two-Stage Combustion of Explosive Mixtures: Ignition Temperature Zones of Heptane-Air Mixtures at Super-Atmospheric Pressures

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The calculations based on the induction period data for the two-stage ignition processes at super-atmospheric pressures show that the effective activation energies, E_{eff}, and the reaction order values, n_{eff}, vary with the ignition temperatures. In two-stage ignition processes at a pressure of 4 atm. and temperature intervals of 240°–310°, 310°–450° and 450°–550°, the respective values of E_{cf} (cf. cold flame) are 36.6; 10.2 and 23.4 kcal/mol. At temperatures in the ignition zone, the values of E_{hf}; n_{hf}, n_{cf}, and Δp_{cf} are negative (hf, hot flame; Δp_{cf}, the maximum increase in pressure in a cold flame process).

A Mechanism of Thermal Decomposition of Ethyl- and Vinyl Iodides and Competition Between Alkyl Halides of the Two Types in the Primary Decomposition Process

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Decompositions of C_2H_5I; C_2H_3I; C_2H_5Br; C_2H_3Br; and C_2H_5Cl in streams of acetone were studied at low pressures and short contact times. Composition analyses of the reaction products show that decomposition of the iodide derivatives is accompanied by a split-off of the iodide atoms and of HI molecules, whereas the decomposition of the other alkyl halides involves the molecular mechanism alone. The activation energy to decompose C_2H_3I is 66.5 kcal/mol. The activation energy of a C—H bond in ethylene—as calculated by assuming that $D(C_2H_3—I)$ is 66.5 kcal/mol—is in good agreement with the experimental value obtained by an electronic impact method.

Investigation of the Mechanism of Formation of Secondary Products in Cracking of Ethane

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A study of C_2H_6 cracking mechanism at 800°–880° and 90 ± 3 mm Hg was carried out in presence of C^{14} radiotracer added as C_2H_4 (0.45%). The study revealed the basic paths in the formation of various secondary products. At the conditions employed, formation of C_3H_8 and C_4H_{10} occurs by recombination of the methyl and ethyl radicals; on the other hand, the C_3H_6 and C_4H_8 are formed by decomposition of the C_4H_9 radical, a $C_2H_5 + C_2H_4$ addition product. In the final analysis, divinyl was obtained by condensation of the ethylene or from its derivatives.

At temperatures of less than 850°, CH_4—which is formed in the system by other than the usual radical reaction mechanisms—plays an important role in the process.

At the conditions investigated, there was practically no reverse hydrogenation of C_2H_4 to C_2H_6.

Investigation by EPR Methods of the Radicals Frozen Out of Exhaust Gases at 77°K

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Properties of the radicals from the exhaust gases in the neighborhood of the combustion zone were determined by an EPR analytical method. Since concentration of the radicals in the effluent gases is too low for direct analyses, the radicals must be accumulated by freezing out at 77°K. The hydrogen atoms, which are present in the gasified product are stabilizable at 77°K as HO_2 radicals. As a result, sensitivity of the EPR method for atomic hydrogen increases at least 50-fold.

Yet, despite high concentrations of atomic hydrogen in the acetylene combustion products, no HO_2 radicals are found on freezing; instead, the radicals present are peroxides of the RO_2 type. The lower concentration limit of the radicals in an acetylene flame is estimated to be 6×10^{10} l/cm³.

Determination by an EPR Method of Fixed Concentrations of Peroxide Radicals in Oxidation of Cumene

By YA. S. LEBED'YEV, V. F. TZEPALOV, AND V. YA. SHL'YAPEENTOKH

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Cumyl peroxide radicals are present in oxidation of cumen over a cobalt stearate catalyst. They are also present when this reaction is initiated by either azo-bis-isobutyronitrol or by dicyclohexyl percarbonate.