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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