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Average Time of Formation of Splinter Ions from *n*-Hexane

L. V. SOOSHEEN, M. V. GOOR'YEV, AND N. N. TOONEETZKY

L. Ya. Karpov Physico-Chemical Institute

A method based on analyses of mass-spectral lines was developed and used to determine the average times of formation of splinter ions. The mean square root periods were determined for formation of $C_3H_n^+$-type ions from *n*-hexane. Despite exaggerating the contributions due to the slow processes, the method proposed yields accurate unbiased decomposition time data. The use of more precise measurements leads to accurate information regarding the nature of the decomposition mechanism.

The Mechanism of Initial Reaction in Oxidation of Methane

A. A. BOREESOV AND G. I. SKACHKOV

Institute of Chemical Physics of the Academy of Sciences of USSR

The experimental data of ignition and isothermal oxidation of methane in air-methane mixtures at atmospheric pressure were analyzed kinetically for small CH_4 conversion values. The results show that at temperatures of about 1,300°, and higher, the rates of CH_4 cracking and oxidation are equal. Comparisons of the rates of oxidation, cracking, and of bimolecular formation of methyl radical indicate that at the temperatures employed the reaction proceeds by the $CH_4 \rightarrow CH_2 + H_2$ route. The curve to correlate the hypothetical average length of the chain produced in the transformation per methyl radical with the reaction temperature, shows a break at about 800°. This is apparently due to changes in the branching and initial oxidation mechanisms for the reacting mixture composition used.

Oxidation-Reduction Reactions of Acceptors in Organic Solvents Exposed to Ionizing Radiation: Reactions of KI and I_2 in Acetone Solutions

M. RODER, GO KOON, N. A. BAKH, AND L. T. BOOGAYENKO

M. V. Lomonosov State University in the City of Moscow

A study was made of the effect of X-rays upon KI and I_2 (in presence of KI) solutions in acetone. The results of irradiation show that in absence of oxygen oxidation of the I^- ions does not occur. Irradiation of the I_2 + KI solutions in vacuum results in disappearance of the iodine, the maximum disappearance, $G(-I_2)$, of 2.1 ± 0.1 eqv./100 ev occurring at I_2 concentrations of 2×10^{-4} M. Irradiation of the KI solutions in presence of oxygen results in oxidation of I^- ions to form I_2. Here, the maximum yield, which occurs at the I_2 concentration of 2×10^{-3} M, is 5.2 ± 0.2 eqv./100 ev. In all cases, the terminal concentrations of I_2 differ from the initial concentrations.

Formation of Free Radicals in Hydrogen Peroxide-Cyclohexanol Reactions

E. T. D'YENEESOV, V. V. KHAREETONOV, AND E. N. RASPOPOVA

Institute of Chemical Physics of the Academy of Sciences of USSR

The formation of free radicals from hydrogen peroxide in hydrogen peroxide-cyclohexanol reaction systems was studied with the aid of inhibitors. The results show that hydrogen peroxide adds-on to cyclohexanol on a mol-for-mol basis. The equilibrium constant, k, of this reversible reaction is $5.4 \times 10^{-6} \exp(7{,}800/RT)$ l/mol. The peroxide addition product formed is "more" rapidly decomposed into free radicals.