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

By S. A. Yantovsky

The State Scientific, Research and Planning Institute for Nitrogen Industry and Synthetic Organic Products

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

By A. E. Sheelov and R. D. Sabeerova

Institute of Chemical Physics of the Academy of Sciences of USSR

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

By A. M. Brodsky, R. A. Kaleen'yenko, K. P. Lavrovsky, and L. V. Shev'yelkova

A. V. Topcheeyev Institute of Petrochemical Synthesis of the Academy of Sciences of USSR

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

By V. N. Panfeelov

Institute of Chemical Kinetics and Combustion of Siberian Division of the Academy of Sciences of USSR

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

Institute of Chemical Physics of the Academy of Sciences of USSR

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.