JOURNAL OF CATALYSIS 5, 549–555 (1966)

Abstracts of Articles Presented in Russian Journal, "Kinetics and Catalysis," Vol. 6, No. 4, July–August, 1965, pp. 577–584. Edited by the Siberian Division of the Academy of Sciences of USSR

Interaction of Atomic Hydrogen with Certain Molecular Compounds in Rarefied Zone of Hydrogen Flame

V. N. Panfeelov, V. V. Voyevodsky
Institute of Chemical Kinetics and Combustion of the Academy of Sciences of USSR

The experimental results presented cover interaction of atomic hydrogen with molecules of some monoatomic alcohols and of some saturated, unsaturated, and aromatic hydrocarbons. The observed decrease in atomic hydrogen concentration in the rarefied zone of the flame due to the added hydrocarbons was determined by EPR technique. Based on these experimental results, the rate constants and activation energies were calculated for the reactions of atomic hydrogen with the molecular hydrocarbons employed in the study. The calculated data are compared with the available published data. Parameter, α, was evaluated and found to be proportional to the ratios of the rate constants of recombination and oxidation of the radical, R.

Mechanism and Kinetics of Thermal Decomposition of Ethane

Yu. I. Koodr'yavtzeva, V. I. V'yed'yen'yeyev
Institute of Chemical Physics of the Academy of Sciences of USSR

The effects of temperatures of 610°–680° and pressures of 10–700 mm Hg were determined on the initial rates of thermal decomposition of ethane. The results show that with decreasing pressure the order of this reaction changes from 1 to 1½. The pressure range corresponding to the alteration in the reaction order is practically independent of the reaction temperature.

A scheme of thermal decomposition of ethane is described. This takes into account the alteration of the magnitude of the monomolecular decomposition constant with pressure. The scheme proposed explains satisfactorily the relationships based on the experimental data.

The Formation Mechanism of Some of the Secondary Products in High Temperature Cracking of Ethane

L. V. Shev'yel'kova, A. M. Brodsky, R. A. Kaleen'yenko, K. P. Zavrovsky
A. V. Topcheeyev Institute for Petrochemical Synthesis of the Academy of Science of USSR

The mechanism of formation of secondary products in cracking C_2H_6 in presence of added (0.01–0.03%) $C_2^{14}H_2$ was studied in a continuous turbulent flow reaction system at temperatures of 830°–920° and a pressure of 90 mm Hg. The results show that C_4H_6 by-product is formed principally by the union of two molecules of C_2H_4. The disappearance of C_2H_2 is mainly via the formation of CH_4 and coke. The rates of these reactions substantially depend upon the character of the heating medium employed. Using quartz as the heat carrier, the CH_4 formed from C_2H_2 does not exceed 3–7%. C_2H_2 participates significantly in the formation of carbonaceous products deposited on the corundum and quartz.

π-Complexes from Radicals and Their Role in Liquid Phase Reaction Kinetics

A. L. Boochachenko, O. P. Sookhanova, L. A. Kalashneekova, M. B. Neiman
Institute of Chemical Physics of the Academy of Sciences of USSR

Aromatic radicals form π-complexes with molecules of the solvents. The complexes so produced either increase or decrease reactivity of the radicals. For cases of decreased radical reactivity, the overall reaction is a combination of the three elementary steps: a free radical reaction, a reaction of the π-complex of a radical, and the reaction comprising equilibration of solvation. The calculated values listed are: equilibrium constants for the π-complexes formed, coordination numbers of the π-complexes, heat of formation of benzene-"dianisyl nitr(ic) oxide" π-complex. Some of the factors responsible for changes in reactivity of the radicals are discussed.