JOURNAL OF CATALYSIS **10**, 95–102 (1968)

Abstracts of Articles in the Russian Journal, *Kinetics and Catalysis*, Vol. 8, No. 2, March–April, 1967. Published by the Siberian Division of the Academy of Sciences, USSR

Use of the Cage Model in Calculating Rates of Bimolecular Reactions in Condensed Phases

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This article proposes a simple method for calculating rates of bimolecular reactions in condensed phases, assuming the existence of two elementary reaction stages: site migrations occurring with a frequency k_m, and cage reactions occurring with a frequency k_i. The kinetic equation so derived affords a good description of the available data on radical recombinations in solids and liquids. In particular, it explains the nature of those segments of the kinetic curves which lie near the origin and which exhibit very high initial rates. The nature of constants k_m and k_i, as well as the possibilities of their determination by experiment, are discussed.

Processes Preceding the Appearance of the Flame and the Ignition of Hydrocarbons as Functions of Their Structure. 1. Delayed Appearance of Cold Flame and Ignition as Functions of Temperature and Pressure

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The authors have studied the delays in the ignition and in the appearance of a cold flame as functions of the temperature and pressure achieved during compression of stoichiometric mixtures of air and various hydrocarbons (*n*-hexane, 1-hexene, cyclohexane, cyclohexene, isooctane, diisobutylene, and a 60:40 mixture of isooctane and *n*-heptane). They have found sharp differences in the nature of the preflame processes and of the delays in ignition occurring in saturated and unsaturated as well as cyclic and acyclic hydrocarbons. Within each of the structural groups, the authors have found a good correlation between its ignition delay temperature relationship and its behavior in internal combustion engines. In particular, the authors have noted the effect of temperature on a tendency toward detonation.

Mass-Spectrometric Studies of Kinetics of Fast High-Temperature Reactions. II. Pyrolysis of Ethyl Formate

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The authors have studied the pyrolysis of ethyl formate at 551–716°C and 12–55 mm Hg by a new technique. The length of the reaction zone was 4 cm. Microsamples of the reaction mixture were withdrawn from that zone via a vacuum line (this immediately "quenched" the sample), and led into the input system of a mass spectrometer.

The degree of conversion of the ethyl formate and the reaction time were determined by the use of an "internal standard." Within the range investigated, ethyl formate decomposes to ethylene and formic acid. The reaction is unimolecular. An equation describing the reaction constant was also obtained.

Kinetics of Polymerization of Ethylene over the $(C_2H_5)_2TiCl_2$-$Al(C_2H_5)_2Cl$ Catalyst Dissolved in Ethyl Chloride

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The authors have studied the kinetics of polymerization of ethylene over the (soluble) catalyst $(C_2H_5)_2TiCl_2 - Al(C_2H_5)_2Cl$, dissolved in ethyl chloride. The reaction temperatures ranged from 10° to 40°C, and the pressures, up to 3000 mm Hg. The polymerization rate is virtually constant over a certain period whose length depends on the temperature, pressure, and catalyst concentration. The rate decreases if the concentration of