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Investigation by a Pulsed Mass-Spectrometric Method of Elementary Processes of Overcharging Thermal Ions on Molecules

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A pulsed method is proposed to investigate the processes operative in overcharging the thermal ions on molecules. Using this method, a study was made of overcharging of Ar⁺, Kr⁺ and Xe⁺ thermal ions on CH4, C2H4, and C2H6 molecules. The results show that in these cases, the value of the rate constant lies between 10⁻⁹ and 10⁻⁸ cm³ sec⁻¹ molecule⁻¹ and that the distribution of intensities of the mass spectra at overcharged conditions practically coincides with that of overcharging by 300 ev the Ar⁺, Kr⁺, and Xe⁺ ions on the same light hydrocarbon molecules. An analysis of the results leads to the conclusion that resonance plays the predominant role in the processes studied. Also uncovered were the reactions involving participation of excited ions $Xe^{+}(^{2}P_{1/2})$.

Effects of Temperature and Pressure on Ignition Delay of Hydrocarbon-Air Mixtures in Adiabatic Compression

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The effects of temperature and pressure on the length of delay in cold and hot flame ignition were investigated in adiabatic compression of 60/40 per cent mixtures of isooctane and n-butane in presence of stoichiometric amounts of air.

The results of this study show that at pressures of over 20 atm both the two-stage preignition and the regions with zero or negative temperature coefficients persist far into the combustion zone. The shape of the ignition region limiting curve depends upon the character of the changes in the duration of the delays within the region. The results obtained lead to the conclusion that evolution of the preignition process occurs with participation of three consecutively competitive reactions, each of which playing a predominant role within a well-defined temperature interval.

Two-Stage Ignition of Explosive Mixtures: Intensities of the First and Second Stages in Ignition of *n*-Heptane-Air Mixtures at Superatmospheric Pressures

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Experimental results are presented on the intensity of two-stage ignition of various air-nheptane mixtures ($\alpha = 1$ and $\alpha = 0.8$). Ignition intensity of each stage depends upon initial processing conditions. The intensities of cold (I_{ct}), blue (I_{bt}), and hot (I_{ht}) flames are 1.04–1.2, 1.3–2, and 2.5–3, respectively. The corresponding amounts of consumed oxygen are 2-6, 14–40, and 50–70%. Of note are the relatively high intensity of the first, "thermo-chain" flame, stage and the low intensity of the second, "blue" flame, stage. A mechanism is proposed for the two-stage process of ignition, to explain it in qualitative terms.

Stage-Wise Addition of Bromine to Propylene at Low Reaction Temperatures

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A bromine-propylene system was investigated thermographically at low bromine addition temperatures. The results show that addition of bromine to propylene occurs via exothermal formation of molecular complexes.

Kinetics of Internal Photoeffect in Organic Semi-Conductors of Anthracene Type

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Compared kinetically are the schemes of singleand double-excitation processes to produce uniform photoeffect in organic semiconductors. Only the double-excitation processes can be shown to explain the experimentally observed kinetics of the photocurrent, the relationship between its fixed values and the intensities of active light and temperature, as well as the energetics of the ionization process.

Investigation of Oxidation Kinetics of Vanadium Trioxide

By V. V. P'YECHKOVSKY AND A. G. Zv'YOZDEEN Polytechnical Institute of the City of Perm

A study of vanadium trioxide oxidation kinetics shows presence of a maximum point on the reaction rate-time curve. In some cases, this point is regarded as indication of autocatalysis. However, in oxidation of V_2O_3 its presence is due to increased rate of reaction as a result of heating up the oxide to a desired temperature.

The formally-derived equations, which are presented, satisfactorily describe the process kinetics within the temperature interval investigated. Reasons are offered to explain the markedly and increasingly diffusion-limited character of the V_2O_3 oxidation reaction at the oxidation levels in excess of 60% and reaction temperatures above 460°.

Apparent activation energy of V_2O_3 oxidation with air was calculated to be 29-37 kcal/mole.

Effects of Imposed Electrical and Magnetic Fields on Catalyst Performance

By P. M. STADNEEK AND E. YU. S'YEKER'YESH Uigorod State University

The effects of imposed electrical field on performance of zinc oxide and zinc oxide—copper catalysts were studied in oxidation of methane. It was found that the processing yields are substantially increased by the imposition of negative voltage.

The effects of imposed magnetic field on catalyst performance were studied, using oxidation of methanol over a silver catalyst as the example. It was found that an imposed magnetic field alone has no effect on the over-all conversion and selectivity characteristics of this catalyst in the reaction. However, simultaneous imposition of magnetic and electrical fields very noticeably alters the formaldehyde yields. The results show that the extent of methanol conversion is largely a function of the size of the angle formed by the lines of the electrical and magnetic fields. EPR Spectra and Nature of Activity of Supported Chromium Oxide Catalysts in Polymerization of Ethylene

By G. K. Bor'yeskov, F. M. Bookana'yeva, V. A. Dzeesko, V. B. Kazansky, and Yu. I. P'yecherskaya

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Catalytic activity of chromium on different supports was evaluated for polymerization of ethylene. The preparations using silica gels and aluminosilicates with minor admixtures of aluminum oxide as the carriers are the most active.

The EPR spectra of each active catalyst invariably signal the presence of Cr⁺⁵ ions. At the same time, for like-based catalysts a correlation exists between catalytic activity and concentrations of pentavalent chromium at the active centers on their surface. Specific activities of dissimilarly-based catalysts are different. This finding and the observed differences in the shape of the EPR signals, lead to the conclusion that the structures of the active centers of dissimilarlybased catalysts are different.

A Mechanism of Interaction of Triethyl Aluminum with Tetrabutyl Titanium and the Structure of Resulting Complexes

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Reaction of $Ti(OC_4H_9)_4$ with triethyl aluminum in deuterated toluene is accompanied by separation of ethane only. This demonstrates that free radicals are not formed in this reduction process.

A study of the spectra in the visible range and of electroconductive properties of the systems with different Al/Ti ratios indicates formation of two complexes:

