JOURNAL OF CATALYSIS 4, 104–108 (1965)

Abstracts of Articles from "Kinetics and Catalysis," Vol. V, Issue 2, March–April, 1964; pp. 201–210. Edited by Siberian Division of the Academy of Sciences of USSR

Determination of an Oxygen-Methane Reaction Rate Constant

By V. V. AZAT'YAN, A. B. NALBAND'YAN, AND TZOOI MEN-YUAN

Institute of Chemical Physics of the Academy of Sciences of USSR

The rate constant of the reaction, $O + CH_4 = OH + CH_3$, was determined by measuring at 570°–660° the primary ignition limits of stoichiometric mixtures of $H_2 + O_2$ and $CO + O_2$, each containing various small amounts of methane. This was found to be

$$(0.94 \pm 0.4) \times 10^{-10} e^{-\frac{8700 \pm 800}{RT}}, \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1},$$

For the reaction, $H + CH_4 = H_2 + CH_3$, at a temperature of 610° the value of the rate constant is 4.9×10^{-14} cm^3 mol^{-1} sec^{-1}.

The mathematical expressions based on the assumed reaction mechanism agree well with the experimental data.

EPR Spectra of HO_2 and DO_2 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

A study was made of the EPR spectra of HO_2 and DO_2 radicals produced in freezing combustion products at a temperature of 77°K. The results show that the individual component widths broaden with increasing concentration of the radicals. Appreciable broadening of the widths may significantly alter the appearance of the spectra. These observations provide the clue to the differences in the EPR spectra of HO_2 radicals as reported by various investigators.

Quantitative Investigations of Radical Reactivity Using a Competing Reaction Method: Phenyl Radical Reactions with Phenol, Aniline, and Anisole

By M. M. BAZEEL'YEVSKY, AND H. S. BAGDASAR'YAN

L. Ya. Karpov Physico-Chemical Institute

The relative rate constants of the phenyl radical reactions with phenol, aniline, and anisole were determined by a competing reaction method. With phenol and aniline in hydrogen split-off reactions, effective values of the constants decrease with increasing concentration. This is due to the combination of molecules of these compounds at the expense of hydrogen bond formation.

The relative constants were also determined for the reactions of hydrogen split-off from the dissociated forms of phenol and aniline and from the associated form of phenol. A discussion covers the causes of high reactivity of hydrogen atoms in phenol and aniline.

Formation of Soluble Complexes of Unsaturated Hydrocarbons with Metal Salts and Their Role in Catalytic Reactions: Thermodynamics of Formation of Soluble π-Complexes of Ethylene with Ag^+ and Cu^+ Ions

By O. N. T'YOMKEEN, A. G. GEENZBOORG, AND R. M. FLEED

M. V. Lomonosov Institute of Fine Chemical Technology in Moscow

The thermodynamics of formation of soluble π-complexes of ethylene with Ag^+ and Cu^+ ions were studied potentiometrically at temperatures of 20° to 80°. The accuracy of this analytical method is demonstrated by good agreement between the experimental and literature data for ethylene-$AgNO_3$ complex formation in aqueous