EDITORIAL NOTE

The Editors of the U.S.S.R. Journal "Kinetics and Catalysis," a Russian language journal, and the Editors of this English language journal have agreed to make available to one another abstracts of their current articles, and to print them in translation for their own journal readers. They hope that this project will be of mutual benefit, a contribution to the scientific community, and perhaps a modest example of peaceful and constructive cooperation.

P. B. W.

Abstracts from Kinetics and Catalysis, Academy of Science, USSR Vol. III, Issue 1, Jan.–Feb., 1962

Dissociation of Ions CH_4^+, CH_3^+, CH_2^+, CH^+, H_2O^+, OH^+ by Single Impact with Atoms and Molecules of Various Gases

By S. E. KOOPRIYANOV

With the aid of a double mass-spectrometer, an investigation was made of dissociation of positive ions with energies of 1500 to 3000 ev. Relative probabilities of dissociation of the ions were determined. It was demonstrated that the spectra of dissociation of CH_4^+, CH_3^+, and CH_2^+ ions depend but little upon the structure of an atom (molecule) which caused their dissociation upon collision; at the same time, the spectra of CH_4^+ and CH_2^+ ions closely resemble the mass spectra of the respective CH_4 and CH_3 molecules.

Conclusion is made that distribution of dissociating ions occurs uniformly in accordance with their excitation energies.

Influence of Solvents on Reactivity and Other Physicochemical Characteristics of Polar Particles. II. Calculation of the Effect of Environment Upon Kinetics of Dissociation of Tertiary Butyl Chloride and Mechanism of the Reaction

By E. S. ROODAKOV

With the concepts of nonspecificity of solvation of reagents and of activated complexes as the background, there is presented an investigation of a quantitative relationship between the properties of a solvent and the kinetics of dissociation (solvolysis) of tertiary butyl chloride. A Grunwald-Winstein equation is derived. Explanation is offered of the exponential dependence of the reaction rate upon the composition of two-component solvents. A suggestion is made to take into account the various fine specific effects of anisotropic solvation in systems of this type. For the same systems, a relationship is derived between the reaction rate and the activity coefficient of the reagent. A method of calculation of the rates of thermal decomposition of gaseous $(CH_3)_3CCl$ is presented, utilizing directly the reaction data for the solvolysis in polar media. Realization of all of the quantitative relationships above is viewed as a direct indication of the unitary nature of the activation mechanism in any media and, specifically, as an indication that in polar media, like in a gaseous one, isobutylene—and *NOT* tertiary butyl cation—is the primary reaction product.

Emulsion Oxidation Under Pressure of Alkyl Aromatic Hydrocarbons. III. Effectiveness of Hydrogen Peroxide in Oxidation of Isopropyl Benzene and of 1,1-Diphenyl Ethane

By R. V. KOOCHER AND S. D. KAZMIN

In the oxidation of isopropyl benzene and of 1,1-diphenyl ethane in alkaline emulsions the initiation of the process by use of hydrogen peroxide is particularly effective during the self-inhibition stage of these reactions. Upon reaction, hydrogen peroxide obviates the reaction-inhibiting factors. An increase in the saturation concentration of hydroperoxide—which is observed at this point—is a function of the magnitude of the inhibiting reaction. The unusual initiating action of hydrogen peroxide occurs in the emulsion oxidation of hydrocarbons because of carrying out this reaction under the specific condition of existence of aqueous phase in the reaction system.

Kinetics and Mechanism of Dimerization of 1,1-Dephenyl Ethylene in the H_2SO_4–H_2O System.

I. Ionization of 1,1-Diphenyl Ethylene in Aqueous Sulfuric Acid

By K. S. Kazanskii and S. G. Entelis

A study of ionization of 1,1-dephenyl ethylene in an H_2SO_4–H_2O system was made by a spectrophotometric method. The concentrations of the H_2SO_4 used were 66 to 80%.

It was shown that the ionization is of a complex nature: the diphenyl-ethyl cation is in equilibrium with two conjugated bases, namely, 1,1-diphenyl ethylene and methyl diphenyl carbinol. The equilibrium constants, K_1 and K_2, for both processes were determined at temperatures of 5°, 20° and 40° and the heats of ionization in either direction were found to be as follows: $\Delta H_1 = 8.1 \pm 1.4$ kcal/mole and $\Delta H_2 = -5.3 \pm 1$ kcal/mole.

The authors give reasons for the belief that the new ionization process, as exemplified by the study described herein, might also be applicable to other aryl olefins.

Kinetics of Thermal Decomposition of Pyroxylin

By G. B. Manelis, U. I. Rubztov, L. P. Smyrnov, and F. I. Doobovitzkii

Study was made of the kinetics of thermal decomposition of pyroxylin gunpowder. The composition of the gaseous products and the heat of thermal decomposition were determined at temperatures of 140°–165°C, both at normal pressure and in vacuum, by measuring heat liberated, the amount of gas formed, and the change in weight of the liquid phase.

It is shown that thermal decomposition of pyroxylin gunpowder consists of primary, secondary, and catalytic reactions; also, that the autoacceleration of thermal decomposition of pyroxylin gunpowder is caused by the formation of gaseous and condensed products.

Calorimetric Study of Reactions of Atomic Hydrogen with Solid Olefins at a Temperature of 77°K

By U. P. Lomanov, A. N. Ponamaryov, and V. L. Talrose

A method has been worked out which permits simultaneous measurement of the rate of consumption of atomic hydrogen and of the rate of heat liberation (up to 10^{-4} cal/sec) in the reaction layer during the interaction at a temperature of 77°K of hydrogen atoms from the gaseous phase with solid hydrocarbons. Using this method, a study was made of the mechanisms for reaction of atomic hydrogen with solid propylene and isobutylene and of recombination of hydrogen atoms in the corresponding alkane layers.

On the basis of the data for reactions of hydrogen atoms with alkyl radicals, an evaluation is presented of the relative role of some of the reactions in the processes of this type.

Recombination of Radicals in Solid Organic Substances. I. Investigation of Defreezing Techniques

By V. K. Yermolayev, U. N. Molin, and N. J. Booben

Using the EPR method, an investigation was made to determine the temperature range in which recombination of radicals occurs during defreezing of various organic substances exposed to fast electrons. It was established that for crystalline substances rapid recombination occurs, as a rule, just before their fusion temperature; on the other hand, for amorphous substances this takes place at their vitrification temperature. With cyclopentane and cyclohexane, the radicals recombine at their polymorphic transition points. For isolated substances it is possible to establish several regions of radical recombination. In the majority of cases, recombination of radicals is, apparently, dependent upon auto-diffusion, which originates in the neighborhood of temperatures of fusion, vitrification, and polymorphic transition points.

The Spectra of Pure Nickel Oxide and of Nickel Oxide-Containing Adsorbed Gases

By K. Kleeyer

The spectra of variously prepared samples of pure nickel oxide and of the oxide containing adsorbed gases were photographed in the wave length range of 3,300–11,000 Å. The spectra were found to agree well with the crystal field theory, provided the value of Dq is taken to be equal to 850 cm^{-1}. Adsorption of oxygen produces a change in the spectrum because of accompanying formation of Ni^{+++} ions. Adsorption of carbon monoxide and of hydrogen results in a different change of the spectrum, which might be explained by the assumption that the Ni^{++} ions on the surface are reduced to Ni^{+}.

A Theory of the Effect of Photoadsorption Upon Semi-Conductors

By F. F. Volkenshtein and I. V. Karpyenko

With the electronic theory of chemisorption as the basis, there are derived the criteria for positive and negative photoadsorption effects (the