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 criteria of photoadsorption and photodesorption) upon semiconductors. The sign of the effect is shown to be dependent upon: (1) properties of the adsorbate and of adsorbent; (2) previous history of the samples subjected to the exposure; and (3) experimental conditions (temperature, pressure). Existing available experimental data are analyzed and interpreted in the light of the theory offered in this paper.

Investigation of Homomolecular Exchange of Oxygen in Presence of Metal Oxides of the Fourth Period. I. Kinetics and Mechanism of the Exchange

By A. P. Dzeesyak, G. B. Boryeskov, and L. A. Kasatkeena

Presented are determinations of the reaction rates, apparent activation energy, and the order of the reaction for homomolecular exchange of oxygen, $O_2^{16} + O_2^{18} = 2O^{16}O^{18}$, in presence of the oxides of the transition metals of the fourth period.

It is shown that the order of activity of the oxides investigated for homomolecular exchange is as follows: $TiO_2 < V_2O_5 < Cr_2O_3 < ZnO < Fe_2O_3 < CuO = NiO < MnO_2 < Co_3O_4$.

The rate of homomolecular exchange is equal to the initial rate of the isotopic exchange between molecular oxygen and the oxygen of an oxide studied. Discussion is presented of possible mechanisms of exchange.

Investigation of Adsorption of Water Vapor on Silica Gel Surface by Nuclear Magnetic Resonance (NMR)

By V. I. Kvleeveedzey, N. M. Yevskaya, T. C. Yegorova, V. F. Keesyelyov, and N. D. Sokolov

Investigation was made of the types of signals produced by nuclear magnetic resonance of the protons of hydroxyl groups which are formed by the water adsorbed on silica gel surface. The results show absence of water molecules on the surface of a sample under vacuum at 200°C. In the initial adsorption stage there were observed sharp diminutions of the width of the band and of the secondary moment. These changes in the signals of NMR are in agreement with the direction of the curves for the differential heats and entropies of adsorption. The results obtained are compared with the data for infra-red spectra. Discussed is the possibility of interaction of water molecules with the surface of silica by the coordinate and hydrogen bonding.

Differences in Catalytic Activities of Platinum and Palladium in Conversions of Cyclohexene and Cyclohexadiene

By V. M. Gryaznov, V. D. Yagodovskii, E. A. Savyelyeva, and V. I. Sheemoolees

The thin layers of platinum and palladium, which were prepared under identical conditions, exhibit sharply different catalytic properties. Dehydrogenation of cyclohexene and of 1,3-cyclohexadiene is the principal reaction over the Pt layer; on the other hand, redistribution of hydrogen takes place over the Pd layer. Capacity of palladium to adsorb much greater amounts of hydrogen is offered as the explanation.

Energies of Bonding of Atoms of Carbon, Hydrogen, and Oxygen of Organic Molecules with Yttrium Oxide

By A. A. Tolstopyatova, I. R. Konyenko, and A. A. Balandin

The values of energies of bonding of carbon, hydrogen, and oxygen atoms of organic molecules with yttrium hydroxide, $Y_2O_3 \cdot nH_2O$, were determined by a kinetic method. A discussion is presented about the cause for carbonization in conversions of alcohols and of hydrocarbons over $Y_2O_3 \cdot nH_2O$; the reason for poor dehydrogenation characteristic of this catalyst is also discussed. A relationship is noted between the magnitudes of the carbon and hydrogen energies of bonding with a catalyst and the ability of various oxides to catalyze dehydrogenation of hydrocarbons. The experimental values of bond energies obtained in this study are used to substantiate the various conclusions made.

Liquid Phase Catalytic Oxidation of Organic Compounds Over Noble Metals. III. Oxidation of Ethylene Glycol to Glyoxal

By I. I. Yoffey, N. V. Kleemova, and A. G. Makeyeff

Liquid phase catalytic oxidation of ethylene glycol over platinum and platinum-palladium catalysts yields glyoxal in up to 15% yields. Other oxidation products formed in the process are glycolic and formic acids, formaldehyde, and glycol-aldehyde.

Also investigated were effects of some of the kinetic parameters upon oxidation of ethylene glycol to glyoxal. Solubility of various carriers was also investigated under the conditions employed in this reaction. The results show that carbon and aluminum oxide are the more stable carriers.