ESR Spectra of Organic Semiconductors Based on Polyvinyl Acetate

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The ESR technique was used to study the products obtained via heat- and radiation-induced modification of polyvinyl acetate, whereby oxygen adsorption by the samples was also investigated. The modified samples exhibit the same paramagnetic and oxygen-adsorption characteristics as similarly modified polyethylene. The product substances are microheterogenous systems, in those regions where polyconjugation dominates alternate with less cross-linked material. Only the surfaces of the regions of polyconjugation adsorb oxygen to any appreciable extent. In products obtained at 500°, 600°, and 700°C, adsorption of one O_2 produces reversible disappearance of two **paramagnetic centers (p.m.c.)**. In products obtained at low temperatures (400°C), the adsorption enhances exchange interactions.

Kinetics of Radiation-Induced Oxygen Chemisorption on γ-Al_2O_3

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The authors studied oxygen chemisorption on γ-Al_2O_3 in radiation fields at 195°–610°K. Two temperature regions were found: In Region I ($T \leqslant 425$°K), the initial chemisorption rate is totally independent of the temperature, and is a strictly radiation-induced, virtually irreversible process of zero order with respect to pressure. In Region II ($T \geqslant 425$°K), the initial chemisorption rate is inversely proportional to the temperature, and the equilibrium pressure is a function of the dose rate. The authors have determined the rate constants and activation energies of some processes, and have proposed several possible mechanisms for chemisorption in Regions I and II.

Polarographic Study of the Effect of Pressure on the Kinetics of Protonization of Pyridine in the Presence of Water

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The authors have studied the effect of pressure (up to 2500 atm) on the kinetics of protonization-deprotonization of aqueous pyridine. They used a polarographic technique whereby the data were obtained in terms of volume catalytic waves in nonbuffered KCl solutions. Correct protonization rate constants can be calculated only from the instantaneous currents generated during the initial interval of life of the first drop. This constant increases with pressure. It was shown that the formation of the activated complex is not accompanied by charge separation. As a result, this complex is solvated to a lesser extent than the ions which are the products of this reaction. Because of this, the rate of the reverse reaction (deprotonization) decreases with the increase in pressure.

Use of the Taft Equation in Selecting Homogeneous Catalysts for the Oxidation of Propylene to Propylene Glycol

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The Taft equation can be used to select organic catalysts with the general formula of RCOOH. Among those catalysts studied were $ClCH_2COOH$, $BrCH_2COOH$, $CHCl_2COOH$, $CHBr_2COOH$, CCl_3COOH, CH_3OCH_2COOH, and $ClCH_2COOH$. The oxidation proceeds via the intermediate formation of peracids RCOOOH and propene oxide. The catalytic activity of the RCOOH compounds, whose calculation takes into account the degree of dissociation of RCOOH in the solution, is primarily determined by the polar constants σ^* and, to a lesser extent, by the steric factors $E_s{}^0$ of the substituent R. Analysis of the calculated rate constants shows that the rate-controlling step is the nucleophilic attack of the olefin on the peracid. The activation energy of the process is 10.2–10.8 kcal/mole. The authors also give a new method of synthesis of $CHBr_2COOH$.

Cyclotrimerization of Butadiene over $C_6H_6 \cdot TiCl_2 \cdot Al_2Cl_6 + R_2AlR'$

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The authors have made a systematic study of cyclotrimerization of butadiene to cyclododecatriene over $C_6H_6 \cdot TiCl_2 \cdot Al_2Cl_6 + R_2AlR'$ (where R is an alkyl group, and R′ is an alkyl group, a halogen or a hydrogen). Under optimal conditions, the yield is 90–93%. Polymerization and trimerization of butadiene proceed simultaneously, and the yield is independent of the reaction time.