

form 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  $460^\circ$ .

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  
*Uggorod 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

*Institute of Catalysis of Siberian Division  
of the Academy of Sciences of USSR.  
Institute of Chemical Physics of the  
Academy of Sciences of USSR*

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 dissimilarly-based catalysts are different.

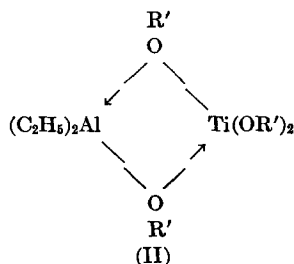
#### A Mechanism of Interaction of Triethyl Aluminum with Tetrabutyl Titanium and the Structure of Resulting Complexes

By T. S. DJABEYEV, R. D. SABEEROVA,  
AND A. E. SHEELOV

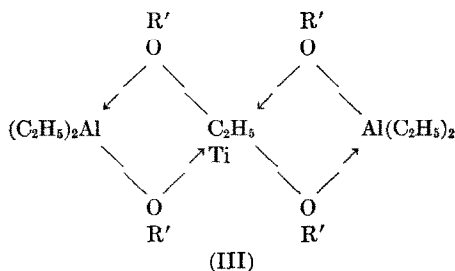
*Institute of Chemical Physics of the  
Academy of Sciences of USSR*

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:



and



Complex III is catalytically active.

The hyper-fine structure of the EPR spectrum of the reaction product points to the interaction of the unpaired electron with the nuclei of two atoms of Al. The complex responsible for this EPR spectrum—and for about 10% of the titanium charged—structurally resembles Complex III, except that OR', rather than C<sub>2</sub>H<sub>5</sub>, stands next to Ti. As would be expected, an identical spectrum was observed in reacting Ti(OR')<sub>3</sub> with (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>AlOR'.

### Reactions of $\alpha$ -Oxides: Investigation of Catalysis by Acids and of the Intermediates of Ethylene Oxide-Carboxylic Acids Interactions

By N. N. L'YEB'YED'YEV AND K. A. GOOSKOV

*N. D. Mend'yeleyev Chemical-Technological Institute in Moscow*

The mechanism of ethylene oxide interaction with carboxylic acids was investigated, using kinetic and spectroscopic analytical techniques. The infrared spectra of an ethylene oxide-acetic acid-potassium acetate system confirmed the formation of binary compounds and of a triple complex. New kinetic data were obtained for the reactions catalyzed by conjugated acids. A mechanism to explain the interaction of ethylene oxide with carboxylic acids is described.

### Mechanism and Kinetics of Acid Catalyzed Conversions of 2-Methylpentene-1

By V. SH. FELDBL'YUM, S. I. KR'YUKOV, AND M. I. FARBEROV

*Scientific Research Institute for Synthetic Rubber Monomers Yaroslavl Technological Institute*

The kinetics of isomerization, dimerization, and hydration of 2-methylpentene-1 were investigated in presence of sulfuric acid as the catalyst. Ex-

perimentally-determined conditions are described for rapid and selective isomerization of 2-methylpentene-1 into 2-methylpentene-2. The isomerization rate constants of the forward and reverse reactions are linear functions of the acidity. This finding agrees well with the concept regarding the course of the reaction in the aqueous phase of the system, assuming: rapid distribution of the olefins between the phases, rapid formation of the  $\pi$ -complexes by the dissolved olefins with protons, and a slow transition of the  $\pi$ -complexes into alkyl cations.

### Catalytic Conversion of Acetylene: Some of the Principles Governing Catalysis by Salts of Acetylene Addition Reactions in Vapor Phase

By A. J. GELBSHTEIN, M. I. SEELENG, G. G. TSHCHEGLOVA, AND I. B. VASEEL'YEVA

*L. Ya. Karpov Physico-Chemical Institute*

Some of the general principles were investigated which govern the character of the heterolytic vapor phase acetylene addition reactions catalyzed by the salts of Hg(II), Cd, Zn, Bi, and of other metals. The discussion presented is based on the experimental data of catalyzed addition to acetylene of molecules of water, HCl, CH<sub>3</sub>COOH, etc.—in vapor phase. The properties of the cations of the catalytic salts are described. The salts whose cations can additively interact with acetylene are the most active catalysts. Taking into account the role of the dative interaction, a study was made of the effects upon the process of the character of the adding molecules, the anions of the salts, and the catalyst carriers.

The possibility of catalysis by protonated acidic complexes is also discussed.

### Kinetics of Oxidation of Ethylene to Ethylene Oxide Over a Selenium-Promoted Silver Catalyst

By V. E. OSTROVSKY, N. V. KOOLKOVA, M. S. KHARSON, AND M. I. T'YOMKEEN

*L. Ya. Karpov Physico-Chemical Institute*

A study was made of the kinetics of ethylene oxidation over a silver catalyst promoted by selenium (0.002 atom %) to stabilize catalytic activity. The procedure of thermally pretreating the catalyst is described. A scheme of the reaction mechanism is presented, along with the support-