solid responsible for the melting is unstable. The equation is

$$V = K(e^{\lambda t} - \lambda t - 1),$$

where V = the volume of gaseous products at time t, and  $\lambda$  and K are kinetic constants incorporating the reaction rate constants. In the vicinity of the m.p. of the starting reagent, the thermal decomposition of pentaerythritoltetranitrate is satisfactorily described by this equation.

### Selection of Catalysts for Homogeneous-Phase Hydrogenation

### A. B. FASMAN AND ZH. A. IKHSANOV The S. M. Kirov Kazakh State University

The authors have investigated the ability of ions of 62 metals to catalyze the oxidation of molecular hydrogen in 70°C aqueous solutions. Ions of elements of groups IA and IB and of platinum metals are capable of homogeneous activation of H<sub>2</sub>. Complexed compounds of platinoid elements and of Cu(II) catalyze the reduction of  $Cr_2O_7^{2-}$ . Noncatalytic oxidation of H<sub>2</sub> takes place in solutions of compounds whose redox potential is higher than +1.4 volts. The author proves that high-activity catalysts for the hydrogenation must be sought among the coordination compounds exhibiting a metal-metal bond.

# Oxidation of n-Butenes and Methylacetylene on Mild Catalysts. Studies Involving Differential Calorimetry

V. P. LATYSHEV AND N. I. POPOVA Institute of Petrochemistry and Coal Chemistry of the Irkutsk State University

Differential calorimetry was used to study the oxidation of a mixture of n-butenes and methylacetylene on a copper and a bismuth-molybdenum catalyst. The catalysis on copper is heterogeneoushomogeneous, while that on bismuth-molybdenum is heterogeneous. It is hypothesized that the mechanism depends on the energies of the bonds between intermediate radicals formed during the reaction and the catalyst surface, as well as on the nature of these intermediate radicals.

### Dehydrogenation of Butane in a Circulating System. 1. Kinetics of Butylene Formation and **Carbon** Deposition

M. N. SHENDRYK, G. K. BORESKOV, AND L. V. KIRILIUK The Giprokauchuk Institute

Dehydrogenation of butane was studied by the circulation technique in a fluid bed apparatus

where the catalyst activity was constant. Initially, the activity of the regenerated catalyst increases, only to fall as a result of carbon deposition. The period during which maximum activity can be maintained depends on the temperature and the space velocity of the butane. It is thought that carbon deposition is a process which parallels the main dehydrogenation reaction.

## Inversion of l-Menthone over a Silica-Alumina Catalyst

E. I. KLABUNOVSKIY, L. F. GODUNOVA, AND A. A. BALANDIN The Zelinsky Institute of Organic Chemistry, Academy of Sciences, USSR

The authors studied the inversion of *l*-menthone to d-isomenthone over a silica-alumina catalyst at atmospheric pressure and 180°-360°C. The studies were done in a flow system, with the space velocity varying from 21 to 144 min<sup>-1</sup>. It was found that at 278°C the degree of conversion of the *l*-menthone over this catalyst does not exceed that previously obtained with a copper catalyst. This phenomenon is apparently due to the protonization of the hydrogen on the copper surface.

# K-Spectra of X-Ray Absorption and the Reactivity of Chelate Copper Compounds

R. G. Akopdzanov, E. E. VAYNSHTEYN, (deceased), N. P. KEYEB, L. M. KAFELI, AND L. F. RUBTSOVA The Institute of Catalysis, Siberian Department, Academy of Sciences,

USSR

The authors have studied the fine structure of K-spectra for X-ray absorption by copper. The copper was in the form of chelate compounds such as 2(0,0) Cu, 2(N,N) Cu, 2(N,0) Cu, 2 (N,S)Cu, as well as in various groups incorporated in the backbones of different monomers and polymers. The authors attempted to evaluate the degree to which ions are involved in the metalligand bond within the chelate moiety of various compounds. They also attempted to quantitatively characterize the effect that various groups, which are in the molecule but are not directly linked to the chelate moiety, have on the ionization of this bond. The authors found a correlation between the reactivity of polychelates and the magnitude of the effective charge concentrated on the copper atom. The reactivity of the polymers decreases with the decrease of the effective charge on the copper and with the increase of the degree to which the copper-ligand bond is ionic.

### Hydrogen Participation in the *cis-trans* Inversions of Dialkylcyclopentanes over Platinum

### O. V. BRAGIN, TAO LUNG-HSIANG, AND A. L. LIEBERMAN The Zelinskiy Organic Chemistry Institute, Academy of Sciences, USSR

The interconversions of cis- and trans-1,2dimethylcyclopentanes over platinized charcoal take place in a stream of pure hydrogen; alternatively, the stream may contain the hydrogen in a mixture with inert gases (He, N<sub>2</sub>, or Ar) and CH<sub>4</sub>. The reaction does not proceed in the absence of H<sub>2</sub>, but the gas need only contain 1% H<sub>2</sub> for the reaction to start; at 3-5% H<sub>2</sub>, the rate becomes significant. Therefore this reaction must be considered bimolecular, since H<sub>2</sub> is a direct participant even though this does not show in the stoichiometric equations. The authors discuss several possible mechanisms and suggest a preferred one, which is formally similar to that of the Walden inversions in  $S_N 2$  reactions.

## Reactions of Propylene Oxide over Various Silver Catalysts. II. Use of Metallic Aluminum Supports

L. M. KALIBERDO, A. S. BAABEL', AND A. A. TORGASHEVA Institute of Petrochemistry and Coal Chemistry of the Irkutsk State University

The authors studied the reactions of propylene oxide over the silver catalyst used for converting propylene to the oxide. They used metallic aluminum supports. By varying the dimensions of support particles and their treatment, they arrived at a catalyst which does not isomerize the oxide in the condition under which the latter is formed (400°C, 0.3 sec contact time).

Oxidation of Pentenes over Copper. 1. Oxidation of Technical-Grade Amylenes over Cuprous Oxide

### YA. B. GOROKHOVATSKIY, A. N. KOROL', M. V. PIŚMENNAYA, E. N. POPOVA, AND A. I. PYATNITSKAYA The Pisarzhevskiy Institute of Physical Chemistry, Academy of Sciences, Ukr. SSR

The authors have studied the partial oxidation of a commercial mixture of amylenes on a cuprous oxide catalyst in the  $320^{\circ}-380^{\circ}$ C range. They have shown that the main products are ethyl acrolein and methyl isopropyl ketone, with acrolein and acetone formed in small quantities. Traces of acetaldehyde, propionaldehyde, and various five-carbon carbonyl compounds were also found. At 340°C, the yield of the partial oxidation products increases with the concentrations of oxygen and amylenes in the mixture, as well as with the space velocity. Carbon dioxide and the C<sub>e</sub>-carbonyl compounds are formed via a parallel or a parallel-consecutive reaction scheme. The authors also propose mechanisms of formation of other products, and give estimates of oxidation resistance of isomeric pentenes.

# Effect of the Energy and Number of Acid Sites of a Silica-Alumina Catalyst on Its Cracking Ability

### D. BARTHOMEUF, M PERRIN, Y. TRAMBOUZE, AND M. PRETTRE Industrial Chemistry Laboratory

Industrial Chemistry Laboratory, University of Lyon, France, and The Institute of Catalysis, CNRS, France

The authors studied two series of silica-alumina catalyst with different degrees of poisoning of proton sites of the surface and different  $Al_2O_s$ contents. The selectivity of the catalyst appears to depend primarily on the energy of the acid sites, rather than on their nature. The activity of these catalysts in cracking reactions also appears to be due to the presence of highly acid sites, since their removal deactivates the catalyst.

### Mass-Spectrometric Study of the Catalytic Redistribution of Hydrogen in Cyclohexene

#### V. I. SHIMULIS AND A. R. SAL'DANYA The Patrice Lumumba University of the Friendship of Peoples

During reaction of cyclohexene vapor over palladium films at room temperature, the curves of accumulation of benzene and hydrogen exhibit a convexity, while that for cyclohexane shows an inflection point. If all hydrogen and other reaction products are continuously removed, the only reaction is dehydrogenation of cyclohexene to benzene. This shows that the only mechanism involved in this "irreversible catalysis," at least under the conditions employed by the authors, is that incorporating consecutive-parallel dehydrogenation and hydrogenation of cyclohexene. Dehydrogenation is not accompanied by the appearance of cyclohexadiene in the vapor.