It was shown that these epoxides can react with caproic acid via the following processes: (*a*) a noncatalytic reaction; and (*b*) reactions catalyzed by trihexylamine or bases, which go via a different mechanism. The authors have derived the kinetic equations for these reactions and have postulated mechanisms involving ring-type and linear transition complexes.

Kinetics and Mechanism of Catalytic Dimerization of Acetylene. I. The Effect of Proton Acidity

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The authors have investigated the effect of NH_4Cl, CuCl, and acetylene on the acidity (h_0) and the concentration of HCl in the solution during the catalytic synthesis of vinyl acetylene. They have derived an equation relating the role of the dimerization to steady-state acidity of HCl at constant activity of cuprous ions. They have also shown that the intermediate of this synthesis is a diacetylenide.

Photolysis of Frozen, Dilute Aqueous H_2O_2

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The ESR analysis of the photolysis of polycrystalline samples of rapidly frozen aqueous H_2O_2 ($[H_2O_2] < 10^{-2}$ moles/liter) at 77°K indicates the presence of a mixture of HO_2 and OH radicals. At $[H_2O_2] = 2 \times 10^{-2}$ mole/liter, only the HO_2 species is recorded. In the range of $10^{-2} - 1$ mole H_2O_2/liter, the quantum yield of stabilized radicals (Φ) is constant. Addition of isopropanol, which is not photolyzed under these conditions, increases Φ. Glass-like frozen samples containing 1.6×10^{-1} mole H_2O_2/liter plus some $NaClO_4$ indicate the presence of the OH species, but their Φ is lower. The authors conclude that the H_2O_2 exists in these frozen solutions as a separate microcrystalline phase and undergoes photolysis independently of the solvent. The increase in Φ upon addition of isopropanol and the decrease in Φ in the glass-like samples are related to the change in the cage effect present in the reaction $H_2O_2 \xrightarrow{h\nu} 2OH$.

Reactions of Atomic Hydrogen in the System, $H_2O + H_2SO_4 + FeSO_4$. V. Effect of Light on "Scavenger" Radicals

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The ESR technique was used to study the effect of light on the "scavenger" radicals of the $\dot{C}_6H_7$ type. It was shown that the ratio of the probabilities of rupture of the C–H and C–D bonds of the >CHD group is approximately the same (3 ± 1) in $\dot{C}_6D_6H$ and $\dot{C}_6H_6D$. The radicals formed by "adhesion" of atomic hydrogen to hydroquinone, pyrocatechol, or benzene sulfonic acid molecules undergo reversible conversions from one radical form to another under the influence of light of two similar wavelengths. The author has compared the long-wave cutoffs in the spectra of the starting molecules with those in the spectra of the radicals formed by "adhesion" and has concluded that the latter always exhibit a shift of the cutoff toward long wavelengths. The shift, $\alpha = \lambda_{\dot{R}}/\lambda_{mol.}$, varies from 1.1 to 2, depending on the structure of the radical.

Reactivity of Pt(IV) Complexes in the Oxidation of CO in Aqueous Solutions

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The authors have studied the reactivity of several Pt(IV) complexes (of the K_2PtX_6 type) in the oxidation of CO, and have found that the reactivity decreases in the following order: $PtI_6^{2-} > PtBr_6^{2-} > Pt(CNS)_6^{2-} > PtCl_6^{2-} > Pt(NO_2)_6^{2-} > Pt(OH)_6^{2-} > Pt(NH_3)_6^{4+} > Pt(CN)_6^{2-}$. This series is the exact opposite of the series formed when the ligands of these complexes are arranged in the order of strengths of the crystalline fields they generate.

Qualitative considerations indicate that apparently there is a reciprocal relationship between the reactivity of the complex and the strength of the Pt–X bond. However, no clear-cut relationship was detected between the reactivities and the stability constants of the above complexes.

Free Radicals Formed by Irradiation of Water and Methanol Adsorbed on Synthetic Zeolites

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The ESR technique was used to investigate the $\dot{H}$, $\dot{O}H$, and $\dot{C}H_2OH$ species formed by γ-irradiation (^{60}Co source, 77°K) of water and methanol adsorbed on type A and X synthetic zeolites.

The authors studied the rates of accumulation of radicals in these systems, and give data on the yield of radicals (G_R) for various percentages of coverage of the zeolite surface. It is shown that radical accumulation in these systems proceeds somewhat differently than during irradiation of free water or methanol at 77°K.

Further, the authors studied the behavior of the radicals when the temperature was raised above 77°K, and found that their stability depends on the structure of the zeolite and the mobility of the adsorbed molecules. The $\dot{O}H$ and $\dot{C}H_2OH$ species recombine via a stepwise mechanism. The annihilation of the $\dot{H}$ radicals is a bimolecular process whose $k_H = 4.2 \times 10^{-16}$ Exp $-[(4600 \pm 800)/RT]$ cm^3/sec.

Thermal Decomposition of Silver Permanganate in the Presence of Metal Oxides

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The authors decomposed silver permanganate at 115°C and showed that ZnO and ThO_2 promote the reaction, that Co_3O_4 and NiO are inert, and that TiO_2 inhibits the process (as do the products of degradation of the silver permanganate itself). The results are explained by assuming an electron exchange between the reactant and the oxide via a layer of reaction product.

The authors have found that $\varphi_1 > \varphi_2 \leqslant \varphi_3$ in the system ZnO–decomposition product–$AgMnO_4$, and that the electrons are transferred from the decomposition product to ZnO and $AgMnO_4$.

An Explanation of the "Distribution Function" in the Theory of Adsorption on Nonuniform Surfaces

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The authors discuss a semiconductor doped with an impurity which does not directly participate in chemisorption, and which is nonuniformly distributed throughout the matrix or on the surface of the semiconductor. It is shown that in this case the Fermi level in the forbidden zone between the energy bands (and, consequently, the chemisorptive properties of the surface) vary in the different areas of the surface. Under these conditions, the surface exhibits unequal heats of adsorption from point to point. The pattern of this nonuniformity depends on the distribution pattern of the impurity. There exists a relationship between the concentration gradient of the impurity and the "distribution function" of the heats of adsorption.

Liquid-Phase Oxidation of Hydrocarbons over Solid Catalysts. I. Paraffins and Cycloparaffins

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Both metals and metal oxides catalyze the partial liquid-phase oxidation of paraffins, aromatics, and cycloparaffins. The activity of oxides is promoted by additives. The authors postulate a heterogeneous-homogeneous mechanism. They also report a new method for control of liquid-phase oxidation (by proper combination of solid catalysts and inhibitors).

Selective Hydrogenation of Crotonaldehyde (to Butyraldehyde)

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Crotonaldehyde was hydrogenated at 100°–180°C at various $H_2:C_3H_5CHO$ ratios and space velocities ranging from 0.2 to 2.2 hr^{-1}. The selectivity with which butyraldehyde is produced is $S_{\text{overall}} = 190.2 + 40\,V - 0.73\,T - 46/x$. The optimum industrial conditions are 150°C, $V = 1$–1.5 hr^{-1}, and a $C_3H_5CHO:H_2$ ratio of 1.

Shift of the Catalyst Potential as a Function of the Rate of Liquid-Phase Hydrogenation. IV. Comparison of Activities of Raney Nickel, and Platinum and Palladium Blacks

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The activities of Raney nickel, and platinum and palladium blacks in liquid-phase hydrogenation were compared in terms of productivity per unit active surface (as referred to hydrogen) and in terms of active surfaces. The productivity factor is specific to each catalyst (and, all other conditions being equal, is determined by the nature of that catalyst).

Activity of Platinum Catalysts. V. Effect of KOH on the Activity of Platinized Carbon

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Catalysts produced by reduction of H_2PtCl_6 with aqueous formaldehyde and KOH (the Zelinsky method) are more active in C_5 dehydro-