

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 ($[\text{H}_2\text{O}_2] < 10^{-2}$ moles/liter) at 77°K indicates the presence of a mixture of HO_2 and OH radicals. At $[\text{H}_2\text{O}_2] = 2 \times 10^{-2}$ 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 $\text{H}_2\text{O}_2 \xrightarrow{h\nu} 2\text{OH}$.

Reactions of Atomic Hydrogen in the System, $\text{H}_2\text{O} + \text{H}_2\text{SO}_4 + \text{FeSO}_4$. 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 $\dot{\text{C}}_6\text{H}_7$ type. It was shown that the ratio of the probabilities of rupture of the C-H and C-D bonds of the $>\text{CHD}$ group is approximately the same (3 ± 1) in $\dot{\text{C}}_6\text{D}_6\text{H}$ and $\dot{\text{C}}_6\text{H}_6\text{D}$. 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, $\alpha = \lambda_{\text{R}}/\lambda_{\text{mo1.}}$, 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: $\text{PtI}_6^{2-} > \text{PtBr}_6^{2-} > \text{Pt}(\text{CNS})_6^{2-} > \text{PtCl}_6^{2-} > \text{Pt}(\text{NO}_2)_6^{2-} > \text{Pt}(\text{OH})_6^{2-} > \text{Pt}(\text{NH}_3)_6^{4+} > \text{Pt}(\text{CN})_6^{2-}$. 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 $\dot{\text{H}}$, OH , and CH_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