Hydrolysis of Vinyl Ethers: Reaction Mechanism in Catalysis Over Mercury Sulfate

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The reaction mechanism of the type, $CH_2 = CH - OX + DOY \rightarrow CH_2 = CH - OY + DOX$, was investigated with the aid of D and ^{18}O, using $HgSO_4$ as the catalyst. In the equation above, X stands for C_4H_9 and CH_3CO, and Y stands for D and CH_3CO. The results show that incorporation of D into the vinyl group does not occur in the course of the reaction. This is the reason for rejecting the concepts of dissociation of vinyl ethers into mercuro-acetylene complexes and, also, of formation of carbonium ions as the intermediates in the processes investigated.

Just as in the case of hydrolysis, the exchange of vinyl acetate with CH_3COOH ($X = Y = CH_3CO$) is accompanied by rupture of the oxygen-vinyl group bonds. Based on the experimental results, the mechanisms are proposed to explain hydrolysis of vinyl ethers and of vinyl exchange reactions which are catalyzed by protons and by $HgSO_4$.

Kinetics and Reactivity of Halogenation of Aromatics in Presence of Metal Chlorides: Reactivity of Aromatic Substances

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Reactivity of a number of aromatic substances was studied in chlorinating them by aluminum chloride dissolved in carbon tetrachloride and in 1,2-dichloroethane. While, from qualitative standpoint, the observed effect due to the substitutes is common to all electrophillic displacements, the effect due to the alkyl groups was found to be abnormally strong as compared to the halogen atoms. The activation energies cannot be directly correlated with reactivity; at the same time, halogenation of alkyl- and halo-benzenes is characterized by a disproportionately low activation energy level and by an activation entropy value which is smaller than that of unsubstituted benzene. These phenomena are, apparently, tied-up with poloraty of the subject compounds and with the solvation effects.

Determination of Catalytic Activity of Nickel-Copper Solid Solution Systems

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Catalytic activity of various nickel-copper alloys was investigated. The alloys studied were prepared by coprecipitation of the metal carbonates, followed by reduction to metallic state. The results of hydrogenation of benzene demonstrate that the alloys containing 10–40% (wt) of copper possess both the greatest catalytic activity (per unit weight of the samples tested) and the greatest surface areas. The specific activities (per unit surface area) and the number of unpaired electrons (determined by magnetic measurements) decrease almost linearly with increasing copper content up to about 80%, dropping sharply at higher concentrations of the copper component. The degree of chemisorption of sulfur-containing compounds (thiophene, carbon bisulfide) on the nickel-copper alloys also changes along analogous curves with increasing copper content.

In hydrogenation of benzene, the energy of activation remains practically constant with all catalytically active alloy compositions.

The relationships noted above substantiate the existence of a direct correlation between the number of unpaired d-electrons in nickel-copper alloys and their catalytic and chemisorptive properties.

Catalytic Ketonization of Acetic Acid Over a Mixed $CaCO_3$—Li_2CO_3 Catalyst

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The kinetics of decomposition of acetic acid to ketones over a mixed $CaCO_3$—Li_2CO_3 (50/50 mol %) catalyst were studied at 374°–435° in a continuous flow unit. The results show that the process activation energy is additive and that catalytic activity of the mixed catalyst is greater than the sum of the fractional component activities. This fact is explained as due to the reaction acceleration which is caused either by the formation of the liquid lithium acetate phase or by structural changes in the activated complex.