Reaction of α-Oxides: Kinetics of Ethylene Oxide–Benzosulfamide Reactions

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A study of ethylene oxide-benzosulfamide interreaction kinetics was carried out using basic catalysts.

In alcoholic solutions two trimolecular reactions of sulfide ions with ethylene oxide occur simultaneously, due to participation of the sulfamide and alcohol. The relationship between the reaction rates and acidity of the alcohol, which is observed, indicates that the third reaction component serves as a donor of protons to the complex which is initially formed by interaction of ethylene oxide with sulfamide ions. In absence of this reaction, the oxidized ring remains closed.

Mechanism and Kinetics of Hydrogen Iodide Addition to Carbon-Carbon Bonds of Compounds in Organic Solvents: Additions of Hydrogen Iodide to Cyclohexene in Hexane and to Toluene in Chlorobenzene Solvents

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The rates of addition of hydrogen iodide to cyclohexene dissolved in hexane and to toluene, in chlorobenzene are described by the kinetic trimolecular equation, below:

$$-d(HI)dt = k_3(C_6H_{10})(HI)(I_2).$$

For the solvents employed in this study, the values of k_3 decrease in the following order: benzene > chlorobenzene > toluene $\approx$ hexane. In a temperature range of 0°–35° the positive temperature coefficient-addition rate curves pass through maximum and minimum points; however, in some other cases the values of these coefficients become negative. With toluene as the solvent, the reaction rate increases continuously with the temperature—although the apparent activation energy of 5.6 kcal/mol is very small. Apparently, the thermal anomaly observed is caused by the formation and decomposition of complexes among the reacting molecules. The values and locations of the maximum and minimum points on the temperature-reaction rate curves are affected by the solvation-desolvation effects.

Kinetic Isotopic Effects of Deuterium and Tritium Exchange Reactions in Hydrocarbon-Base Systems

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The kinetic isotopic effects (KIE) in deuterium and tritium exchange reactions were determined for the following two-component hydrocarbon-base systems: indene, fluorene, methyl-β-naphthylketone *and* water-free methylamine; indene *and* liquefied ammonia; toluene, benzene, naphthalene *and* a solution of potassium amide in liquefied ammonia. The experimentally determined KIE values approach those calculated by assuming complete rupture of the reacting bond of the intermediates. A mechanism of hydrogen exchange with bases is also discussed.

Photolysis of Ethyl Alcohol Solutions at a Temperature of 77°K

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The EPR studies of kinetics of accumulation, disappearance, and interconversion of the radicals formed in ultraviolet ($\lambda > 2400$ Å) irradiation of ethyl alcohol solutions of H_2O_2 and C_6H_6 were carried out at a temperature of 77°K. The formation of C_2H_5, CH_3, CH_3CHOH and CH_3CH_2O radicals was substantiated by an EPR method. The results show that the light in a specified wave length range decomposes the alcoholic radicals to form C_2H_5 and CH_3 radicals. Switching-off the light leads to gradual reconversion of these radicals to the CH_3CHO and CH_3CH_2O alcoholic radicals.

Other results of this study show that the light of greater than 3600 Å wave length isomerizes the CH_3CH_2O radicals into CH_3CHOH radicals and that raising the temperature to 110°C reverses this reaction at a marked rate.

The results of mass-spectrometric analyses show that CO, CH_4, and H_2 are the principal products in the photolysis of H_2O_2 and C_2H_5OH solutions.