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Diquantum Photoionization of N,N-Dimethyl-n-Phenyldiamine in Alcohol Matrix at 77°K

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The initial rate of photoionization of N,N-dimethyl-n-phenyldiamine in an alcohol solution is proportional to the square of intensity of light. An investigation of the effect of interrupted lighting shows that the characteristic life-time of the intermediate particles in the reaction is identical with that of an amine molecule in a triplet state. Thus, the subject reaction represents a novel example of the "true" diquantum photochemical reaction due to adsorption of light by a molecule in a triplet state.

Reactions of α-Oxides: Reactivity of Phenols with Ethylene Oxide and the Reaction Kinetics

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An investigation of the kinetics of interaction of phenols with ethylene oxide in an alcoholic solution shows that the process is a sum-total of two reactions: in one of these, the free phenol is the proton-donating agent; in the other one, this function is performed by the alcohol. This finding explains the Patap-Voyteh's data and demonstrates inadequacy of the Boyle-Marle's results on reactivity of phenols, since these follow the straight line relationship of Hammet's equation only in the reaction where an alcohol serves as the proton donor. With free phenols as the donors, the reactivity-phenol acidity log-log plot does not obey the straight-line relationship but, instead, forms a curve passing through the minimum point at $K_A = 10^{-5}$.

The reaction mechanism proposed assumes that interruption of the oxidation cycle occurs only by the simultaneous action of the nucleophilic agent (phenolate) on the carbon atoms and of the proton-donating agent (free phenol, alcohol), on the oxygen atoms of the oxide.

Limiting Product Yields in Liquid Phase Oxidation of Xylene

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In oxidation of n-xylene (a by-product of a coking process), the limiting product yields are directly proportional to cobalt stearate catalyst concentrations of the order of 10^{-4} mol/l. The reaction is retarded by accumulation of the catalyst poisons.

Kinetics of Radiative Polymerization of Allyls

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In radiative polymerization of allyl alcohol, either alone or in the alcohol-water azeotropic mixture, the conversion rate (a) remains constant, regardless of magnitude of the polymer yield; (b) is directly proportional to the dosage; (c) is greater in the aqueous solution than in the pure state; (d) decreases with decreasing reaction temperature.

Activation energy of the polymerization reaction is temperature-dependent, increasing from \sim /kcal/mol at -78° to \sim 7 kcal/mol at 300° —with the alcohol in either the pure state or in the aqueous solution. In this temperature range, the radiation-chemical yield of the polymer increases with temperature from about 10° to 10° mols/ 100° ev.

The dilatometric curves and the polymer yield data are shown for radiative polymerization of seven allyl monomers.