BASIC ASPECTS OF PHOTOCATALYTIC DETOXIFICATION OF ORGANIC HALOGENS BY TiO₂ NANOCRYSTALLITES. PHOTOLYTIC AND RADIOLYTIC INVESTIGATIONS.

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Various forms of TiO₂ (nanocrystallites in colloid solutions, powders and layers) are considered as promising photocatalysts for detoxification of persistent organic chemicals which are present as pollutants in waste water effluents from industrial manufacturers and even from regular households. Such pollutants penetrate and reach water sources and must be removed or destroyed in order to prevent damage to people or to the environment. Some of the toxins, such as organic halogenated compounds is difficult to remove by moderate chemical redox reactions, but can be mineralized by a free radical mechanism. Pilot plants for detoxification of industrial wastes on TiO₂ surface are currently being tested in several countries. In view of this recent development it is of particular interest to investigate yields of the reactive intermediates and reaction mechanisms of reactions of representative organic substrates. Such work is presently going on in many laboratories. In the present contribution we focus on the nature of the primary oxidizing species and the possible ways to increase photolytic yields, with particular attention to chain reactions in organic halogen compounds.

Although the work concerns photocatalysis, radiation chemistry may provide useful results regarding kinetic parameters and comparative tests. Thus, comparison between photocatalytic (TiO₂), radiolytic and chemical hydroxylations of phenol provides evidence that the reactive hydroxylation agent is an OH• radical adsorbed to the TiO₂ surface. The initial photochemical products are conduction band electrons and valence band holes in the TiO₂ nanocrystallites, which become “trapped” within less than 30 ps. Reactions with substrates adsorbed to the surface initiate a sequence of reactions which may be complicated, depending on the nature of the substrate. In most cases reactions of holes are faster than reactions of electrons. Direct capture of the mobile electrons and holes requires that the scavenger be adsorbed at the TiO₂ surface. In the presence of appropriate hole scavengers, reductive dehalogenation takes place by a chain reaction mechanism producing very high yields of chloride ions, although the initiation reactions usually have quantum yields of only a few percents at most.