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Generation of Organic Radicals During Photocatalysis on TiO₂¹

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It is well-known that water-related radicals (such as OH· species) are produced by charge transfer events at UV-irradiated TiO₂ surfaces. In contrast, organic radicals are generally viewed as being formed by reactions with OH· groups and not by direct charge transfer events. Using rutile TiO₂(110) as a model photocatalyst, we show that organic radicals are generated in single-step charge transfer events during photodecomposition of adsorbed carboxylates and ketones. Some organic radicals (e.g., methyl) are ejected from the surface and, in high surface area catalysts, experience reactions away from the surface of origin. Other radicals (e.g., ethyl and t-butyl) have limited ability to escape the surface of origin without capture and subsequent thermal reactions. Understanding the chemistry associated with organic radical formation on TiO₂ opens the door for more detailed examinations of charge transfer dynamics and energy redistribution during photon-initiated reactions important to heterogeneous photocatalysis.

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