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Origin of coverage dependence in photoreactivity of carboxylate on TiO_2(110) surface. IGOR LYUBINETSKY, Oregon State University, ZHITAO WANG, MICHAEL HENDERSON, Pacicfic Northwest National Lab — Employing scanning tunneling microscopy (STM) and ultraviolet photoelectron spectroscopy (UPS), we have observed a strong nonlinear decay of the reaction rate constant with coverage for the photolysis of trimethyl acetate on TiO_2(110). This effect was not linked to intermolecular interactions of TMA but to the accumulation of the coadsorbed bridging hydroxyls (HO_b) deposited during (thermal) dissociative adsorption of the parent, trimethylacetic acid (TMAA). Confirmation of the hindering influence of HO_b groups was obtained by the observation that HO_b species originated from H_2O dissociation at O-vacancy sites have a similar hindering effect on TMA photochemistry. Though HO_b's are photoinactive on TiO_2(110) under ultrahigh vacuum conditions, UPS results show that these sites trap photoexcited electrons, which in turn likely (electrostatically) attract and neutralize photoexcited holes, thus suppressing the hole-mediated photoreactivity of TMA. This negative influence of surface hydroxyls on hole-mediated photochemistry is likely a major factor in other anaerobic photochemical processes on reducible oxide surfaces.

Igor Lyubinetsky
Oregon State University

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