PHOTO-TAUTOMERIZATION OF ACETALDEHYDE TO VINYL ALCOHOL: A NEW MECHANISM FOR ORGANIC ACID FORMATION IN THE TROPOSPHERE

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We present a detailed kinetic master equation (ME) model of the photochemistry of acetaldehyde under conditions relevant to tropospheric chemistry. The dissociation and isomerization rate constants are benchmarked to collision-free experiments in a supersonic expansion, at wavelengths where reaction is only possible on S_0. Extensive photo-isomerization is observed when irradiated with actinic ultraviolet radiation (310-330 nm). The ME model quantitatively reproduces the experimental observations and shows unequivocally that keto-enol photo-tautomerization, forming vinyl alcohol, is the crucial first step.

When collisions are included into the ME, the model quantitatively reproduces the previously reported quantum yields for photodissociation at all pressures (0 - 1 atm) and wavelengths (295 - 340 nm). Crucially, at 1 atm pressure, and averaged over the intensity distribution of the solar spectrum, our model predicts that 26% of the total CH_3CHO quantum yield is into the collisionally-relaxed vinyl alcohol photo-tautomerization product.

The photochemistry and photophysics of many carbonyls are similar to that of acetaldehyde. Therefore, we expect that photo-tautomerization of carbonyls into their respective enols will be a general phenomenon under atmospheric conditions. Such photo-tautomerization mechanisms are not included in any current tropospheric model and might, given that an enol will react rapidly to form an acid, we propose that they may account for the production of organic acids in the troposphere.