

The fast photo-dynamics of the aqueous formate ion.

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We have used femtosecond transient absorption spectroscopy to investigate the primary reaction dynamics of the aqueous formate ion, $\text{HCOO}^-(\text{aq})$, following photoexcitation at 200 nm. Using probe pulses covering the spectral range from 200 to 620 nm, we find that the most abundant photoproduct is the oxygen radical anion, $\text{O}^-(\text{aq})$, which suggests that the formate ion dissociates predominantly into the $\text{HCO}+\text{O}^-$ channel. Previously, we have reported on the primary photodynamics of aqueous formic acid where photoexcitation at the same wavelength produced the OH radical as primary photoproduct which suggested photodissociation into the $\text{OH}+\text{HCO}$ channel¹. However, in both cases we have been unable to detect the formyl radical which indicates that a rapid hydration of HCO takes place by water molecules of the solvent cage. We observe distinct differences in the recombination dynamics for the cases of the formate ion and formic acid in correspondence with the energetics of the photofragments.

¹ J. Thøgersen, S.K. Jensen, O. Christiansen and S.R. Keiding, "Fast photo-dynamics of Aqueous Formic Acid", *Journal of Physical Chemistry A* **2004**, 108, 7483