



Matteo Rini, Ben-Zion Magnes, Ehud Pines and Erik T. J. Nibbering, *Science* **301** (5631), 349-352 (2003).

“Real-time observation of bimodal proton transfer in acid-base pairs in water”

The main point of the paper is as follows:

Until now the Eigen-Weller mechanism of acid-base reactions, that has been used since decades, has been understood to comprise 1) diffusional motion of acid and base, 2) “on-contact” reaction dynamics where a proton is transferred from the acid to the base, and 3) diffusional separation of proton transferred ion pairs. Numerous studies have found a relatively slow “on-contact” reaction rate (on the order of $10^{10} \text{ M}^{-1}\text{s}^{-1}$), with an “on-contact” distance with typical values of 6-8 Å, that always appears to be larger than the sum of the radii of the reaction partners.

We now have revealed the reason for these findings by using a) an state-of-the-art femtosecond infrared spectroscopic method where we follow proton transfer in real time by monitoring both acid **and** base vibrational marker modes, and b) a comparison of our results obtained on samples with high and with low base concentrations. It follows that under conditions of high base concentrations we are able to monitor proton transfer along pre-existing hydrogen bonds in “tightly” bound acid-base complexes, where an extremely rapid proton transfer was found. In contrast for low base concentrations we observe initially uncomplexed acid, that upon diffusional motion, forms “loosely” bound complexes with a much slower reaction time. We are thus led to refine the Eigen-Weller model by use of a three-stage mechanism that exists of 1) diffusional motion of acid and base, 2) formation of a “loosely” bound acid base encounter pair, 3) rearrangement to a “tightly” bound reaction pair, followed by 4) a prompt proton transfer reaction. This refined reaction scheme is shown in Fig. 4 of our paper.

Since acid-base neutralization is one of the most fundamental chemical reactions, that not only occurs in liquid water, but also in proteins (e.g. enzyme catalysis, or proton pumps through membranes), we are confident that our achievements will attract general interest. In particular our findings of a different reaction time scale between “tightly” and “loosely” bound acid-base pairs will have a major impact for the theoretical modelling of proton transfer in liquid water.