Please cite this article in press as: Sülzner, New light on proton transfer: Spectral and kinetic signature of a transient Eigen complex, Chem (2024), https://doi.org/10.1016/j.chempr.2024.10.017

Chem

CellPress

Preview

New light on proton transfer: Spectral and kinetic signature of a transient Eigen complex

Niklas Sülzner[1,*]

Despite the long-lasting research on proton transfer as a fundamental chemical reaction, not all details regarding its precise mechanism have been revealed. Particularly, a complete spectroscopic and kinetic characterization of all intermediates remains challenging. In the September issue of *Cell Reports Physical Science*, Lee et al. identify a transient Eigen complex and determine the molecularity of each elementary step.

Proton transfer (PT) as the center of Brønsted acid-base theory is one of the most elementary yet also ubiquitous reactions in chemistry and many of its related fields.[1] Examples—to name only a few—range from acid-base catalysis in synthesis, over technical applications like the development of proton membranes for fuel cells, to the rich field of biochemical systems. Importantly, proton transfer can also take place in an electronically excited state, referred to as excited-state proton transfer (ESPT), with the ESPT of anthocyanin pigments that prevent plants from photodamage as an interesting example from nature. Thus, PT is really omnipresent in chemistry and of general importance.

To study the kinetics of proton-transfer reactions, so-called photoacids have established as particularly powerful tools during the last decades. These photoacids are molecules that exhibit an acidity increase upon electronic excitation[2]; i.e., they are more acidic in an electronically excited state, usually the lowest-lying (singlet) state, S_1, compared to the (singlet) ground state, S_0. Therefore, irradiation with light can trigger an ESPT from the photoacid to its surroundings, allowing monitoring of the kinetics of the ESPT using time-resolved spectroscopy, e.g., if a pulsed laser is used as a light source.

Many previous studies have investigated the kinetics of the ESPT in water, particularly using the famous photoacid HPTS (8-hydroxypyrene-1,3,6-trisulfonate) as a probe.[3] Reaching back to the pioneering work by Eigen and Weller in the 1950s,[4,5] the proton-transfer mechanism shown in Equation 1 has become generally accepted.

$$\begin{aligned} &AH_{(aq.)} + B_{(aq.)} \\ &\rightleftharpoons [AH\cdots B]_{(aq.)} \\ &\rightleftharpoons [A^-\cdots HB^+]_{(aq.)} \\ &\rightleftharpoons \left[A^-\cdots (H_2O)_n\cdots HB^+\right]_{(aq.)} \\ &\rightleftharpoons A^-_{(aq.)} + BH^+_{(aq.)} \end{aligned}$$

(Equation 1)

The following species are included (from top to bottom): reactants: acid (AH) and base (B); intermediates: reactive encounter complex ([AH···B], CPX), contact/hydrogen-bonded ion pair ($[A^-\cdots HB^+]$, CIP/HBIP), solvent-separated ion pair ($\left[A^-\cdots (H_2O)_n\cdots HB^+\right]$, SSIP; involving n water molecules); products: corresponding base (A^-) and acid (BH^+). The index (aq.) indicates the respective solvation shells.

According to this mechanism, which is nowadays referred to as the Eigen-Weller model, the following sequential steps are involved (assuming both AH and B are neutral):

(1) Encounter of the Brønsted (photo)acid AH and base B under formation of a reactive encounter complex (CPX);
(2) (Fast) proton transfer within the CPX yielding a contact ion pair (CIP) or hydrogen-bonded ion pair (HBIP), bound by Coulomb interactions between the corresponding acid BH^+ carrying the proton and the corresponding base A^-;
(3) Stepwise separation of the HBIP by diffusive intrusion of solvent molecules, generating various solvent-separated ion pairs (SSIPs) as additional intermediates;
(4) Subsequent separation into the fully separated (or free) ion pair (FSIP, FIP).

Existing studies have primarily focused on the ultrafast, initial PT (step 2), extensively probed by a multitude of time-resolved spectroscopy techniques (e.g., transient UV/Vis, IR, X-ray absorption; Raman scattering; fluorescence emission). On the one hand, precise analysis of the full mechanism is difficult in protic solvents (including water and alcohols) due to short lifetimes of the intermediates caused by the extensive hydrogen-bond (HB) network that enables high proton conductivity. On the other hand, the focus on the initial PT had been also retained by the development of super-photoacids, i.e., exceptionally strong photoacids with negative excited-state pKa values,[6] which

[1]Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, 44801 Bochum, Germany

*Correspondence: niklas.suelzner@rub.de

https://doi.org/10.1016/j.chempr.2024.10.017

All rights are reserved, including those for text and data mining, AI training, and similar technologies.

Please cite this article in press as: Sülzner, New light on proton transfer: Spectral and kinetic signature of a transient Eigen complex, Chem (2024), https://doi.org/10.1016/j.chempr.2024.10.017

started a race toward increasingly fast ESPT in the literature.

In contrast, no extensive HB networks exist in aprotic solvents, which, by definition, lack HB donation, leading to longer lifetimes of the intermediates in line with slower proton diffusion. Moreover, further differences in the ESPT mechanism arise in the special case of cationic photoacids (AH^+). Since the corresponding bases A of these photoacids are charge-neutral, no HBIP, but a so-called Eigen complex (EC), is formed upon the PT (cf. step 2 in Equation 1) that is predominantly bound by charge-dipole rather than charge-charge interactions. While the separation of the HBIP occurs via diffusion under the influence of the Coulomb interaction that facilitates reprotonation (i.e., geminate recombination), the separation of the EC mostly resembles a simple Brownian motion. Consequently, for cationic photoacids in aprotic solvents, the Eigen-Weller model can be thought of as being terminated at step 3 (Equation 1), missing additional intermediates. This termination step, which could not be studied in protic solvents before, becomes accessible in aprotic solvents, but had not been addressed until recently.

The article by Lee et al. in the previous issue of *Cell Reports Physical Science* reports on the kinetic details of the different mechanistic steps during the ESPT of the super-photoacid *N*-methyl-7-hydroxyquinolinium (NM7HQ+) in binary mixtures of acetonitrile with dimethyl sulfoxide (DMSO) as a cosolvent, with a special focus on the molecularity of the dissociation of the involved Eigen complex.[7] They could show that an efficient ESPT under these conditions involves pre-coordination of one solvent molecule (acting as the base) to the photoacid already prior to excitation since the formation of this encounter complex is a kinetic bottleneck. After ESPT within the encounter complex, the separation of the Eigen complex requires a second solvent molecule, yielding the free excited corresponding base and a Zundel-type complex comprising the proton and two DMSOs. Thereby, this article exactly fills the above-mentioned gap regarding information on the termination step in the Eigen-Weller model, with some important implications as described in the following.

A main consequence concerns the direct comparison with similar work in other aprotic solvents. For example, neutral HPTS-based super-photoacids have been recently investigated with great care regarding the ESPT to a phosphine oxide in acetonitrile as well as the ESPT to solvent in acetone-water mixtures.[8,9] In contrast to the photoacid NM7HQ+ studied by Lee et al., these hydroxypyrene photoacids are neutral and thus no EC, but instead an HBIP, is formed during initial PT. However, no significant contributions from geminate recombination (*vide supra*) had been observed, nor had a distinction between an SSIP and F(S)IP been attempted.[8] Despite the difference in the intermediate (EC vs. HBIP), both photoacids should be comparable. In particular, for the related solvent acetone, similar observations compared to those by Lee et al. have been made, i.e., evidence for formation of a photoacid-water complex prior to excitation in the ground state and indications for the involvement of additional water molecules in the CPX dissociation (one additional molecule) and HBIP separation (less than one additional molecule).[9] Thus, a similar Zundel-like hydronium ion as in DMSO appears to be involved in acetone, but neither a discrete assignment of the molecularity nor the direct separation had been addressed.

More generally, the work by Lee at al.[7] has first a conceptual consequence: it demonstrates the incompleteness of the conventional Eigen-Weller model that neglects information regarding the molecularity of the individual reaction steps. Secondly, it showcases a similarity between ESPT in protic and aprotic solvents: in both environments cooperativity between the solvent molecules is key to proton stabilization. This cooperativity leads to the direct involvement of a second solvent molecule for aprotic solvents (due to restricted hydrogen bonding), while it is the collective effect of many molecules for protic solvents that ultimately allows for proton hopping as described by the famous Grotthuss mechanism. For the latter, the cooperativity also manifests in the involvement of solvent wires for proton transport (as e.g., studied by the same authors).[10] Thirdly, since the assignment of the structure of the protonated solvent cluster (here, the Zundel-type ion) is based on quantum-chemical calculations, this work presents a successful example of a combined experimental-theoretical study on photoacids. Lastly, this work has the potential to become relevant in practice since DMSO is an organic solvent that has recently become more popular in synthesis, calling for new insights for understanding the mechanisms of other reactions.

In summary, Lee et al. report an interesting observation of an Eigen complex between the photoacid NM7HQ+ and DMSO in acetonitrile solution. While such transient species are typically rare due to short lifetimes, the authors succeed with a characterization using time-resolved spectroscopy and determine the molecularity of each step in the ESPT mechanism based on kinetic analysis. Due to the impact of these results for the understanding of proton transfer in aprotic solvents, we look forward to new, insightful results in the future, also from theoretical studies.

ACKNOWLEDGMENTS

N.S. thanks the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation)–388390466–CRC/TRR 247 (Project A05) for financial support.

DECLARATION OF INTERESTS

The author declares no competing interests.

Please cite this article in press as: Sülzner, New light on proton transfer: Spectral and kinetic signature of a transient Eigen complex, Chem (2024), https://doi.org/10.1016/j.chempr.2024.10.017

REFERENCES

1. Chou, P.-T., and Solntsev, K.M. (2015). Photoinduced Proton Transfer in Chemistry and Biology. J. Phys. Chem. B *119*, 2089. https://doi.org/10.1021/jp510024r.

2. Agmon, N. (2005). Elementary Steps in Excited-State Proton Transfer. J. Phys. Chem. A *109*, 13–35. https://doi.org/10.1021/jp047465m.

3. Nandi, R., and Amdursky, N. (2022). The Dual Use of the Pyranine (HPTS) Fluorescent Probe: A Ground-State pH Indicator and an Excited-State Proton Transfer Probe. Acc. Chem. Res. *55*, 2728–2739. https://doi.org/10.1021/acs.accounts.2c00458.

4. Eigen, M. (1964). Proton Transfer, Acid-Base Catalysis, and Enzymatic Hydrolysis. Part I: ELEMENTARY PROCESSES. Angew. Chem. Int. Ed. *3*, 1–19. https://doi.org/10.1002/anie.196400011.

5. Weller, A. (1959). Outer and inner mechanism of reactions of excited molecules. Discuss. Faraday Soc. *27*, 28–33. https://doi.org/10.1039/DF9592700028.

6. Tolbert, L.M., and Haubrich, J.E. (1994). Photoexcited Proton Transfer from Enhanced Photoacids. J. Am. Chem. Soc. *116*, 10593–10600. https://doi.org/10.1021/ja00102a028.

7. Lee, S.-H., Choi, Y.-J., Kim, Y.-J., Kee, J.-M., and Kwon, O.-H. (2024). Capturing an Eigen complex in an acid-base reaction shows step-resolved molecularity. Cell Rep. Phys. Sci. *5*, 102155. https://doi.org/10.1016/j.xcrp.2024.102155.

8. Grandjean, A., Pérez Lustres, J.L., and Jung, G. (2021). Solvent-Controlled Intermolecular Proton-Transfer Follows an Irreversible Eigen-Weller Model from fs to ns. ChemPhotoChem *5*, 1094–1105. https://doi.org/10.1002/cptc.202100177.

9. Sülzner, N., Geissler, B., Grandjean, A., Jung, G., and Nuernberger, P. (2022). Excited-State Proton Transfer Dynamics of a Super-Photoacid in Acetone-Water Mixtures. ChemPhotoChem *6*, e202200041. https://doi.org/10.1002/cptc.202200041.

10. Choi, Y., Kim, H., and Kwon, O. (2022). Acid–base reaction of a super-photoacid with a cooperative amide hydrogen-bonded chain. Bull. Korean Chem. Soc. *43*, 501–507. https://doi.org/10.1002/bkcs.12479.