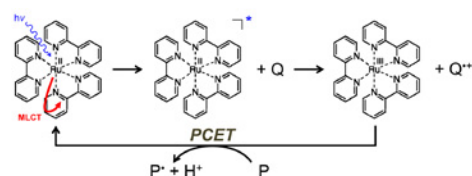


Transient absorption spectroscopy studies of proton-coupled electron transfers

Abstract

On the course to sustainable energy, artificial photosynthesis is one of the greatest scientific challenges of our time. From a chemist point of view, the understanding of proton-coupled electron transfers which take place during the process is a fundamental issue. To decipher them, transient absorption spectroscopy, applied to model systems, is a method of choice. General methods and most recent results obtained by this technique are the object of the present review.



Keywords

Photochemistry • Transient absorption spectroscopy • Proton-coupled electron transfer • Reaction mechanisms

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1. Introduction

Reactions in which an electron and a proton are transferred together are called proton-coupled electron transfers (PCET) [1-4]. The particularity of such reactions is that the electron and the proton are transferred to different centers, unlike H-atom transfer (HAT) in which both elements reach the same reaction center [5,6]. PCET reactions are the cornerstone of many fundamental processes, in particular photosynthesis (natural or artificial) [7-15], and are of fundamental interest for the description, development and enhancement of chemical systems related to energy conversion [16] and small inert molecule activation such as water oxidation [17-20] or carbon dioxide reduction [21-24]. These two key examples involve multiple proton-electron transfers (Table 1) which are of extremely high complexity. To our knowledge, no experimental mimicking system is able to tackle efficiently such multiple processes, and most of the work accomplished aimed at describing in details one proton-one electron transfers. More generally, there is an incredibly high demand on understanding such reactions at the molecular level [25], for establishing fundamental models as well as for developing scaled systems, thus enhancing the growth of the field and the number of dedicated studies in the last years.

Looking at the molecular aspect of PCET reactions, two types of mechanism can take place (Figure 1): one corresponds

to the transfer, during the same elementary step, of both the electron and the proton, in what is called concerted proton-electron transfer (CPET); on the other hand, the two particles can be transferred one after the other, corresponding to two stepwise mechanisms, with the electron transferred first (electro-proton transfer, EPT) or the proton transferred first (proton-electron transfer, PET) [26-29]. Thermodynamically, the two stepwise mechanisms are unfavoured because they generate high-energy intermediates (namely radical anion or cation, *i.e.* highly reducing or oxidizing species) which are costly to stabilize. On the opposite, in the concerted pathway, no such intermediate

Table 1. Examples of reduction reaction involving a proton transfer and their apparent standard potential [7,30].

Reduction Reaction	E°' (V vs NHE, pH = 7)
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	-0.82
$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$	-0.61
$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$	-0.52
$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O$	-0.48
$2H^+ + 2e^- \rightarrow H_2$	-0.41
$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$	-0.38
$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$	-0.24

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is present, but the fact that the two particles are transferred concertedly, including a “heavy” proton, counterbalances the gain in energy by a (possibly important) kinetic counterpart.

A significant amount of work has been accomplished in order to understand and describe the parameters which control the nature of the mechanism taking place for a particular reaction in a specific set of conditions, having in mind that the three possible pathways are in competition for most systems. The common manner to decipher this is to modulate parameters such as the pH, the concentration of base or/and buffer (if present), the temperature or the driving force of the reaction by changing the nature of the oxidant for example.

From an experimental point of view, a large panel of techniques is employed for the study of PCET. For example, recent works were published based on electron paramagnetic resonance (EPR) [31,32] or UV resonance Raman (UVRM) [33,34], but more generally electrochemical techniques [27,35], among which cyclic voltammetry, and time-resolved absorption spectroscopy, with the laser-flash triggering of the reaction, are used. The aim of the present review is to describe in details the latter in the particular framework of the study of PCET reactions, to present a state of the art of experimental procedures (compounds employed such as photosensitizers, quenchers, samples preparation, etc.), to detail the way data are obtained and analyzed and finally to sum up the most recent results obtained by this powerful experimental technique.

2. Experimental Procedures

A method of choice to study PCET reactions is to generate, with photons, an initial oxidizing species which will start the whole reaction chain (Figure 2). For that, the first compound required is the photosensitizer, whose role is to initiate the chemical process by converting photons into chemical energy by the intermediary of its excited state. However, proton and electron transfers described here are related to molecules in their electronic ground states, whereas PCET reactions can also be achieved with molecules in their electronic excited states [36-39]. Even if dealing with similar concepts, this is not the purpose of the present review. The most common compounds used in this goal

are the tris(bipyridine)ruthenium(II), $[\text{Ru}(\text{bpy})_3]^{2+}$, and its related compounds, which present a lot of valuable characteristics for the photochemist. For the parent compound $[\text{Ru}(\text{bpy})_3]^{2+}$ for example, the absorption spectrum is located in the visible, with an intense peak at 452 nm ($\epsilon_{452} = 14600 \text{ M}^{-1} \text{ cm}^{-1}$) [40]. It is very photostable and significantly soluble both in aqueous solution and in polar organic solvent; upon blue irradiation (up to 550 nm), a singlet excited metal-to-ligand charge transfer ($^1\text{MLCT}$) state is formed which is converted within few tens of femtoseconds by intersystem crossing (IC) into a triplet excited state ($^3\text{MLCT}$); the remarkable thing about the IC is that the global efficiency of the singlet-triplet conversion is close to unity and that the triplet state formed is long-living ($\tau \sim 600 \text{ ns}$ in neat water at 293 K), long enough to be quenched and to initiate chemical reactions. Having in hand a long-lived excited state is important, but to easily be able to observe its evolution, it is even better to have a strong absorption, which is the case with $[\text{Ru}(\text{bpy})_3]^{2+}$ since the difference in absorption coefficients between the ground and the

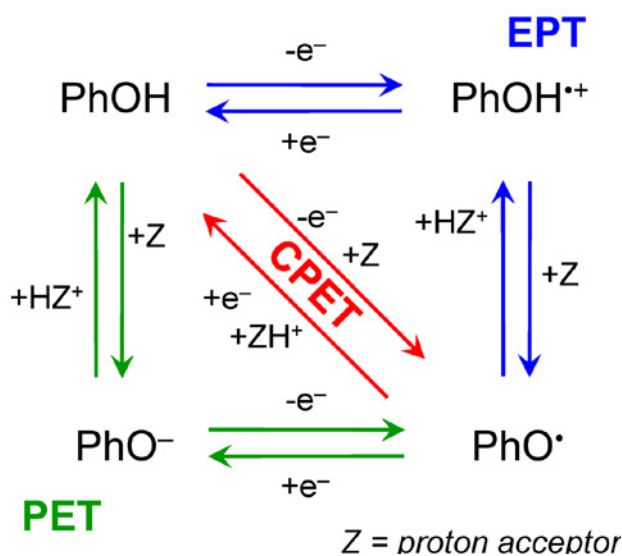


Figure 1. Stepwise (blue and green corners) and concerted (red diagonal) mechanisms for proton-coupled electron transfers, with the example of phenol (PhOH) oxidation. EPT, PET and CPET: see text.

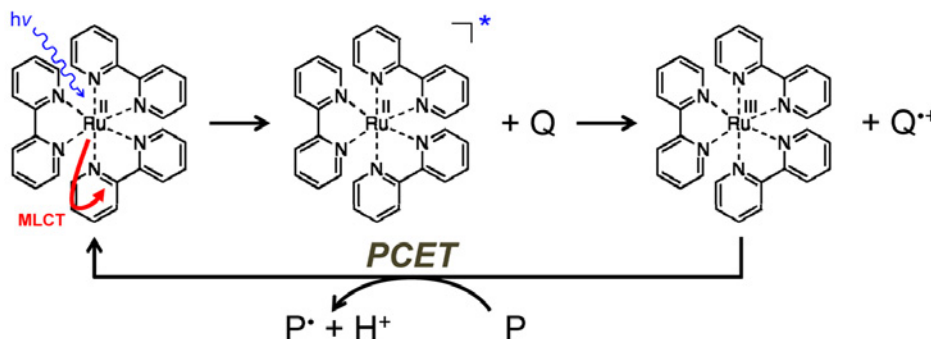


Figure 2. Schematic view of photoinduced proton-coupled electron transfer. $\text{Ru}^{\text{II}}(\text{bpy})_3$ = photosensitizer, Q = quencher, P = compound being proton-coupled oxidized.

excited state was lastly reported to be $\Delta\varepsilon = -10000 \text{ M}^{-1} \text{ cm}^{-1}$ at 452 nm [41], resulting in a huge signal bleach observed in the blue side of visible region after flashing the compound with a laser. Furthermore, reduced and oxidized forms of $[\text{Ru}(\text{bpy})_3]^{2+}$ (i.e. 1+ or 3+ states) are adjacent (see Table 2), opening the possibility of an oxidative as well as a reductive quenching. Last but not least, $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ is easily available in high purity at a relative low cost. Another interest of Ru(bpy) analogs is the ability to tune their redox properties easily by functionalizing the bpy ligands with various groups, such as short alkyls, esters, hydroxides, and so on. By using such several slightly different complexes, one has the possibility to keep the optical properties of Ru(bpy)s but also to benefit a (possibly large) range of driving force for the PCET reaction. For example, when adding two methyl groups to bpps, the redox potential shifts from +1.26 down to +1.09 V vs NHE, whereas when adding one carboxylate ester to two of the three bpps, the redox potential shifts up to +1.47 V vs NHE [42].

Other transition metal complexes can as well be employed instead of ruthenium complexes, for example containing rhenium such as complexes based on rhenium pentacarbonyl $[\text{Re}(\text{CO})_5]^+$, which possess interesting properties of photooxidant [43] and more particularly of excited-state oxidant [44]. Rhenium was also used for intramolecular generation of tyrosyl radical with the great advantage not to need an external quencher [45]. Metalloporphyrins, for example containing zinc, were also used as photosensitizer in some PCET studies [46-48]. Some time ago, Shafirovich *et al.* extensively studied PCET reactions in DNA, particularly guanine oxidation, by direct UV-photolysis of DNA samples [49-52].

As a source of photons, researchers have used lasers for decades. Thanks to technical enhancement, very compact all-solid state lasers are now available at accessible costs. These lasers are robust, stable, all-computer controlled and do not really need to be tuned frequently, rendering them routinely usable by chemists. To optimize the use of such set-ups, the addition of an optical parametric oscillator (OPO) to the system is highly valuable and makes it more flexible. For example, with a typical Nd:YAG laser frequency tripled at 355 nm, it is possible to generate wavelength from UV to near-IR (typically from 400 to 2500 nm) with an OPO, giving the ability to selectively excite a given compound or to study the effect of different initial excitation energy.

Once the initial excited state is formed, one needs to take advantage of it by the use of an excited-state quencher, sometimes called “flash-quencher”. Its role is to convert as much as possible of the initial excited species into another reacting species which will ignite the chemical reaction. For this, researchers typically employ high concentrations of quencher (several millimolar or tens of millimolar) compared to excited state species (typically tens of micromolar) to maximize the quenching reaction by tending to the diffusion limit. In this strategy, one of the most widely used quencher is methyl viologen dichloride (MV^{2+} , 2Cl^-). Despite its relative low purity commercially available (generally 98%), it has the great advantage to be converted, upon one-electron reduction, into an easily identifying (large absorption band peaking at 605 nm)

Table 2. Reduction potentials for Ru(bpy)₃ redox couples in water [53,54].

Couple	E° (V vs NHE)
$\text{Ru}(\text{bpy})_3^{3+} / \text{Ru}(\text{bpy})_3^{2+}$	+1.26
$\text{Ru}(\text{bpy})_3^{2+*} / \text{Ru}(\text{bpy})_3^+$	+0.84
$\text{Ru}(\text{bpy})_3^{3+} / \text{Ru}(\text{bpy})_3^{2+*}$	-0.84
$\text{Ru}(\text{bpy})_3^{2+} / \text{Ru}(\text{bpy})_3^+$	-1.26

and strongly absorbing ($\varepsilon_{605} = 13700 \text{ M}^{-1} \text{ cm}^{-1}$) [55] radical cation ($\text{MV}^{•+}$). This way, in addition to the typical bleaching recovery of the ruthenium photosensitizer, another observable species is available (Figure 3). The reverse side of the medal is that inside the reaction cage between the excited photosensitizer and the quencher, a back electron transfer is possible, and in some cases it is pretty efficient. So the overall quenching process can be lowered since the fraction of species escaping the reaction cage usually is far from being a hundred percent. For example, the cage escape yield for the typical system Rubpy- MV^{2+} is only ca. 0.25 [56], so with a concentration of Rubpy around 50 μM , a concentration of MV^{2+} around 25 mM, and an excitation energy between 5 and 10 μJ per pulse, only ca. 4 μM of the oxidizing $[\text{Ru}(\text{bpy})_3]^{3+}$ are formed [42].

Several other possibilities exist in the choice of the quencher. Pentaaminocobalt(III) trichloride ($\text{Co}(\text{NH}_3)_5^{3+}$, 3Cl^-) presents the advantage of making the back electron transfer impossible since its one-electron reduction leads to the loss of an amino ligand. However, this compound is photosensitive and hard to purified, so its use is somehow problematic. Hexaamineruthenium(III) trichloride ($\text{Ru}(\text{NH}_3)_6^{3+}$, 3Cl^-) is also an interesting quencher since it does not have any significant absorption in the visible, in both (II) and (III) forms, and has a higher cage escape yield than with methyl viologen. However, the lack of absorption signature does not allow the observation of its kinetic behavior and thus it should be compared with another quencher to ensure that no other side reaction takes place in addition to the quenching one.

Finally, once formed, the reduction product of the quencher, for example methyl viologen radical cation, undergoes its own chemistry such as radical-radical recombination which must be taken into account in the whole reaction scheme. However, the timescale of such secondary reactions is generally (much) longer than the timescale of the process of interest and so it can be reasonably neglected in general.

Apart from purely bimolecular systems in which the oxidizer and the species being oxidized are individual molecules, (supra)molecular assemblies of the two elements made by covalent linking or hydrogen-bonding (“dyads” or “triads”) were developed by several groups [57-65]. Such a strategy is interesting since it prevents diffusional issues by linking the

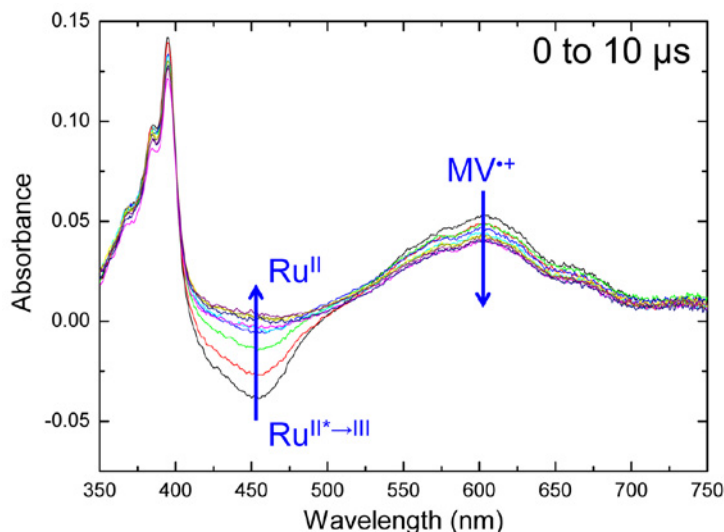


Figure 3. Typical transient absorption spectra in the microsecond timescale measured in an aqueous buffered solution (phosphate buffer at 0.01 M, pH = 7) containing 50 μM of $\text{Ru}(\text{bpy})_3^{2+}$, 25 mM of MV^{2+} and 25 mM of phenol. The bleaching recovery of the photosensitizer is observed at 450 nm and the transient absorption decay of the radical cation of the quencher at 605 nm.

“donor” and the “acceptor”. In this kind of systems, the electron transfer is intramolecular, whereas the proton transfer can be either intramolecular, to an internal acceptor, or intermolecular, *i.e.* to an external base or to the bulk.

Finally, particular care must be taken regarding dissolved gases. Oxygen is known to be a quencher for the $\text{Ru}(\text{bpy})_3^{2+}$ excited state, significantly shortening its lifetime and thus fading the efficiency of quenching. Its reactivity towards other products generated in the reaction (radical ions, radicals) must also be prevented. On the other hand, when we conducted measurements in pure water, we observed that even the very small proportion of CO_2 in air was able to drift the pH of pure water samples. So, a systematic and careful purge of the solutions with argon for *ca.* 15 minutes is necessary, as well as maintaining a slight argon flux all along the preparation of the samples, for example during the pH adjustment. The use of a septum-sealed cuvette is, in that sense, highly recommended too.

3. Data Acquisition and Analysis

Data acquisition in transient absorption spectroscopy is of two types: spectral measurements are usually obtained by the use of a charge coupling device (CCD) camera at a given delay time after the laser flash; kinetic measurements are obtained by the digitalization of an electric signal coming from a photomultiplier tube (PMT) at a given wavelength by an oscilloscope. It is also possible to obtain spectral information using a PMT by “reconstructing” a spectrum from kinetics traces, but generally with a lower quality than with a camera. Conversely, it is possible to obtain kinetic information from a set of spectra, but once again with a poor level of precision.

Both type of data are obtained by averaging a certain number of data single acquisition, in order to increase the signal/noise (S/N) ratio. Typical optical densities obtained with moderate laser

energy (a few mJ per pulse) and usual concentration of $\text{Ru}(\text{bpy})_3^{2+}$ (50 μM for an optical pathlength of 1 cm) are in the order of 10 mOD. Having in mind that detection systems typically have a baseline noise of 0.5 to 1 mOD (lower detection limit), a number of 10 to 20 averages is the common rule. Further increasing the number of averages generally does not increase the S/N ratio significantly but it does increase the number of laser shots in the sample, making possible a degradation of the system which could interfere with the measurement and bias the results.

Kinetic traces measured by such methods are then analyzed thanks to a kinetic model and its related equations. Since solutions are used to conduct the experiments, one has the possibility to tune the concentration of reactant(s), particularly the oxidized species concentration, to render the kinetic law a pseudo-first order one. However, in most cases, side reactions of generated products take place, for example when radicals are formed in the oxidation of phenol-type molecules. These radicals are known to dimerize, but with a rate constant low enough to be decoupled from the PCET reaction, or even to be neglected as mentioned above.

Once kinetic traces are collected, the rate constant is extracted by fitting the (average or single) kinetic trace of the photosensitizer, for example a ruthenium complex in the following equations. Once in its Ru^{III} oxidized form after flash-quenching (by compound Q, see Figure 2), it can return to Ru^{II} state by back electron transfer (BET) with $\text{Q}^{\cdot+}$ or it can oxidized compound P, as expressed in equation (1a). However, in most cases, experiments are realized with an excess of compound P, and this excess greatly increases the apparent rate constant of the proton-coupled oxidation, making the BET negligible, so the fitting law can be assumed to be a pseudo-first-order one, as showed in equation (1b). The apparent rate constant k_{app} is then divided by the concentration of the compound of interest P to obtain the net rate constant of the proton-coupled oxidation

(equation (2)). However, in some cases, in particular when the PCET driving force is pretty low, the apparent rate constant can be of the same order of magnitude than the BET rate constant, a situation that makes impossible the use of a monoexponential fit. To take into account the contribution of the BET, a correction factor must be added to the kinetic law, after measuring the rate of the BET in a set of experiments without the compound P, as expressed in equation (3) (for the full explanation of kinetic equations, see supporting information of ref. [42]).

$$-\frac{d[\text{Ru}^{\text{III}}]}{dt} = k_{\text{PCET}}[\text{Ru}^{\text{III}}] \times [\text{P}]_{\text{total}} + k_{\text{BET}}[\text{Ru}^{\text{III}}] \times [\text{Q}^{\cdot+}] \quad (1a)$$

$$-\frac{d[\text{Ru}^{\text{III}}]}{dt} = k_{\text{app}}[\text{Ru}^{\text{III}}] \quad (1b)$$

$$k_{\text{PCET}} = \frac{k_{\text{app}}}{[\text{P}]_{\text{total}}} \quad (2)$$

$$[\text{Ru}^{\text{III}}] = \frac{[\text{Ru}^{\text{III}}]_0}{1 + k_{\text{BET}}[\text{Q}^{\cdot+}]_0 \times t} \exp(-k_{\text{app}} \times t) \quad (3)$$

Finally, having in hands a collection of rate constant for a range of driving force, pH, temperature, base concentration, etc., one must design a reaction scheme (Figure 4) to propose a reaction mechanism and to identify the parameters driving it.

4. Recent Results

In the last years, several studies were conducted on the proton-coupled oxidation of phenol and phenol-type molecules [66-68].

First because in the natural photosynthesis, a key primary step is the oxidation of a tyrosine residue in the Photosystem II subunit [17,32], which still represents a great source of motivation for several research groups. Secondly, phenolic compounds (especially radicals formed upon oxidation) are involved in a large variety of enzymatic processes, for example in ribonucleotide reductase (RNR) [69-71] or cytochrome c oxidase [72-76], but also in DNA oxidation, damage and repair reactions [77-79] or in polyphenol free-radical scavenging [80]. In addition, the oxidation of phenol leads to an important increase in its acidity (from pKa = 10 to -2 for phenol for example) [81,82], thus inducing the release of the proton to a nearby base or directly to the bulk, making it a suitable model to study PCET reactions. PCET mechanisms are also involved in redox reactions at metal oxide surfaces, as was demonstrated by a combination of experimental techniques including transient absorption for TiO₂ and ZnO particles [83], which are of great interest for energy conversion or photocatalysis.

In our group, we conducted extensive efforts to decipher the main parameters controlling the PCET oxidation of phenol, by evaluating the influence: of a change in the driving force of the reaction, using different ruthenium photosensitizers; of the presence, or not, of a base (such as hydrogen phosphate in buffered solutions or a typical N-containing base such as pyridine) and the evolution of the rate constant with its concentration; of switching from H₂O to D₂O thus measuring the kinetic isotope effect (KIE) which is often considered as a piece of evidence in favor of the concerted pathway; of the temperature, giving further insights into the thermodynamics of the reaction,

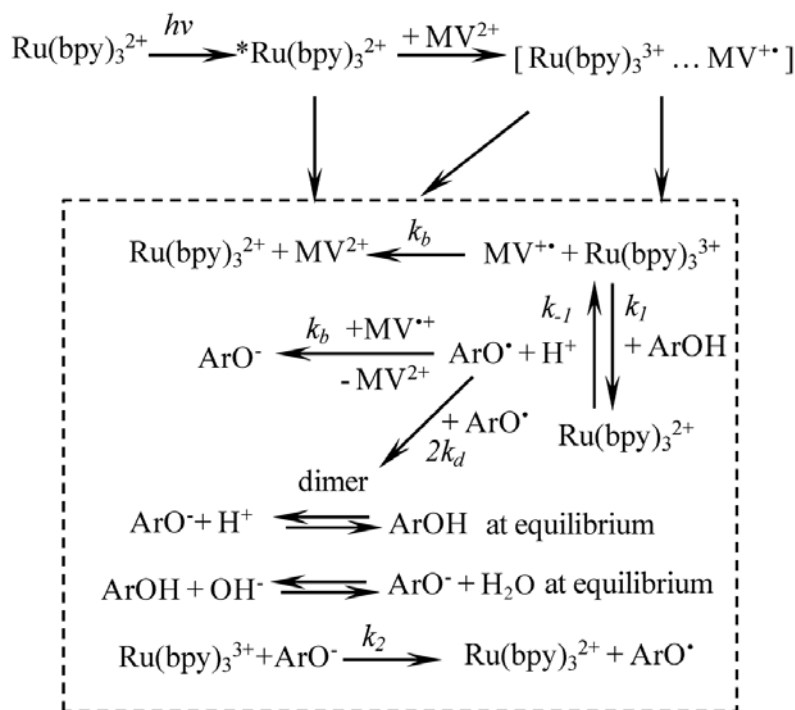


Figure 4. Reaction mechanism scheme for the flash-triggered concerted proton-coupled oxidation of phenol. The dashed square stands for the limit between photophysical events (outside) and chemical reactions (inside) [42]. ©2010 by National Academy of Sciences.

such as the reorganization energy [42,84,85]. Our conclusions, based on transient absorption spectroscopy studies, and in line with electrochemical studies [86-88], were the following: in pure water, without any base present in solution, the oxidation of phenol at low pH (below ca. 5) is pH-independent and was shown to correspond to a concerted pathway (CPET) with water as the proton acceptor and thermodynamically controlled by the counter-diffusion of the reaction products; a higher pH, the mechanism was demonstrated to be stepwise, with the proton transfer first (PET) and with hydroxide ion being the proton acceptor [42]. In the presence of a base, such as phosphate or pyridine, we demonstrated that the mechanism of phenol oxidation was concerted as well, and we were able to show that the intrinsic (*i.e.* at zero driving force) proton acceptance efficiency was the best for water itself [84]. We illustrated this conclusion by evaluating the proton solvation radius from reorganization energies we calculated, and we obtained the largest cluster in the case of pure water, corresponding to the delocalization of the proton on several water molecule whereas the solvation radius corresponds to one hydrogen phosphate molecule when present, or one pyridine surrounded by a few water molecule in the last case [85].

Other groups conducted similar transient absorption studies, in particular recently on tyrosine [64,89,90] and tryptophan [91,92] oxidation, either by bimolecular reaction or by intramolecular reaction when the compound is covalently linked to the photosensitizer. Barry and co-workers conducted several studies on redox-active tyrosines by EPR and UVRP, with connection to Photosystem II and RNR, deciphering the role of water molecules network and the effect of the oxygen evolving complex oxidation on the PCET reactions of tyrosine [31-34].

Following previous studies on their model system constituted of a ruthenium complex covalently linked to a tyrosine residue (Ru-Tyr) [93-97], Hammarström and co-workers pursued their investigations by evaluating the dependence of the concerted PCET rate constant on the proton transfer distance thanks to the attachment on the assembly of a conjugate base [89]. They were thus able to emphasize the critical importance of H-bonding. They also extended the pH range of study for the Ru-Tyr model compound, concluding that four different mechanisms could be defined for the tyrosine oxidation in four pH intervals [90]. They conducted similar studies on the oxidation of tryptophan, either bimolecularly or when covalently linked to the photosensitizer, and came to the same conclusion, *i.e.* tryptophan is oxidized concertedly with the proton release to the bulk [91,92].

Their analysis of the kinetics is, at this point, still highly debatable because it is based on an "unusual" pH-dependence of the rate constant at intermediate pHs which is explained by a pH-dependence of the reaction driving force [98], a problematic concept since the driving force of the reaction is governed by the *standard* potential and thus do not depend on pH. Another factor may have been considered with great attention: the participation of the base form of the buffer, even at small concentration, which could play the role, at least in part, of proton acceptor, in complement to water. In their first studies and analysis [96],

they underestimated this point, but they later mentioned that the buffer could explained the pH-dependence observed [92]. These assessments simply show that more studies must be undertaken, even for model systems such as those described above, to be able to unambiguously describe PCET reactions kinetics and mechanistic schemes.

After previous articles presenting the methodology and preliminary results [38,99], Stubbe, Nocera and co-workers studied the temporal monitoring of radical transport into the $\alpha 2$ subunit of RNR by transient absorption by incorporating a rhenium photooxidant in a short peptide mimicking *E. Coli* RNR [71]. They showed that an efficient radical transport injection and propagation in the subunit, a process which involves PCET, is requiring the presence of a hydrogen-bond network between two tyrosine residues. These results underlined the key role played by the geometry of the system in the occurrence and efficiency of radical transport in natural systems.

Recently, using flash photolysis and transient absorption measurements, the kinetics of triplet state quenching of 3,3',4,4'-benzophenone tetracarboxylic acid (BPTC) by DNA bases in aqueous solution has been reported [78]. By observing the BPTC ketyl radical and exploring the evolution of the rate constant with pH, a stepwise proton-coupled electron transfer has been proposed for thymine oxidation. Another work demonstrates the role of hydration in the DNA cleavage upon visible irradiation of a ruthenium quinone-containing complex without dioxygen [100]. Unlike other metal complexes considered for photodynamic therapy, which work as DNA cleavage agents by activation of cellular dioxygen to form reactive oxygen species, the complex studied in this paper shows that the ligand hydration can induce an effective DNA cleavage in hypoxic conditions via a PCET.

5. Conclusions

Photosynthesis is a fascinating process, in which plants and algae convert light into chemical energy stored in organic molecules. The basic scheme - water oxidation in one side, carbon dioxide reduction in the other side - is so simple that it makes it understandable by everyone, even if it is still facing researchers, thus being an exciting playground for chemists. It also represents great challenges because behind the apparent simplicity of the whole process, different levels of complexity are hidden. In that sense, artificial photosynthesis is a very active and diverse area of research [101], with crucial implications in the actual global energy issues we are faced with [102-104].

In this great story, fundamental chemistry, whose goal is to describe and to understand basic processes and the parameters that control them, is needed to (ultimately) develop scaled systems able to produce source of renewable energy in the near future. In this line, proton-coupled electron transfers are of fundamental interest, and many processes, natural or not, are now described using this framework. Experimental PCET studies can be conducted by various techniques, but

transient absorption spectroscopy is a method of choice thanks to its sensitivity, its time resolution and the flexibility of recent optical systems in terms of excitation wavelengths, excitation energies or detection tools. Associated with molecular design, creating various complexes of different

redox potentials, of tunable donor-acceptor distances, with defined spatial organization, etc., spectroscopic studies such as transient absorption ones will, without a doubt, significantly contribute to the fulfillment of the understanding of artificial photosynthesis.

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