Photochemistry

Deutsche Ausgabe: DOI: 10.1002/ange.201607176
Internationale Ausgabe: DOI: 10.1002/anie.201607176

Tuning Excited-State Reactivity by Proton-Coupled Electron Transfer

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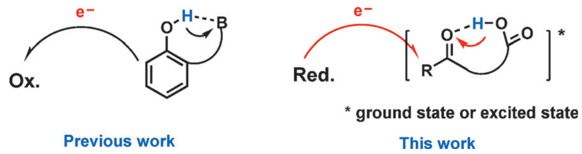
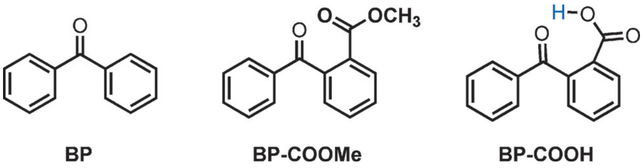
Dedicated to Professor Thomas J. Meyer on the occasion of his 75th birthday

Abstract: *The reactivity, and even reaction pathway, of excited states can be tuned by proton-coupled electron transfer (PCET). The triplet state of benzophenone functionalized with a Brønsted acid (^{3}*BP-COOH) showed a more powerful oxidation capability over the simple triplet state of benzophenone (^{3}*BP). ^{3}*BP-COOH could remove an electron from benzene at the rate of $8.0\times10^5\,\text{M}^{-1}\,\text{s}^{-1}$, in contrast to the reactivity of ^{3}*BP which was inactive towards benzene oxidation. The origin of this great enhancement on the ability of the excited states to remove electrons from substrates is attributed to the intramolecular Brønsted acid, which enables the reductive quenching of ^{3}*BP by concerted electron–proton transfer.*

Proton-coupled electron transfer (PCET) reactions involve the concerted transfer of both an electron (ET) and a proton (PT). These reactions play a vital role in energy conversion and photocatalysis.[1–3] Notably, concerted PCET is thermodynamically more favorable than the stepwise ET–PT pathway, as it could avoid the formation of high-energy intermediates,[1,4] and thus improve the energy conversion efficiency in natural photosynthesis.[4,5] In artificial photosynthetic systems, one critical step is to use excited-state electron transfer to create oxidative and reductive species for driving fuel-production reactions such as water splitting to form oxygen and hydrogen.[6–8] The formation of charge-separated (CS) states in this process relies on the redox properties of the light absorber in both the excited and ground states.[9] The reductive quenching of an excited state by PCET reagents[10,11] and PCET oxidation by chemical oxidants and electrodes[12–16] have been investigated to mimic events that occur naturally in photosystem II. The rate of recombination decay of the CS state was shown to be significantly reduced by the introduction of PCET.[17,18] The importance of PCET is also becoming increasingly apparent in developing new catalysts and improving the efficiency of the integrated molecular assemblies.[19]

We report herein a novel example of tuning excited-state reactivity by proton-coupled electron transfer. In previous work, phenols that bear a basic functional group were extensively used as model complexes for understanding the mechanistic details of PCET.[12–16] Our strategy in this work is to create a counterpart to the previously investigated model complexes (Chart 1). We selected benzophenone functionalized with a carboxyl group as model complex (Scheme 1), based on the following considerations: 1) the triplet excited electronic states of benzophenone derivatives are commonly used as hydrogen-atom abstractors or electron acceptors in photoreactions;[20] 2) benzophenone acts as an electron acceptor and therefore requires a pendant acid, whereas phenols act as electron donors and therefore were equipped with a pendant base; 3) benzophenone bearing a carboxyl group might undergo PCET from an electronically excited state. Interestingly, this strategy leads to a significant improvement of the redox properties of both ground state and excited state, and a switch of mechanism in the reaction between the excited state and hydrocarbons was observed from hydrogen-atom transfer (HAT) to PCET.





Scheme 1. The structures of benzophenone (BP) derivatives used in this work.

The cyclic voltammogram of methyl-2-benzoylbenzoate (BP-COOMe) in acetonitrile shows a quasi-reversible redox couple at −2.19 V vs. Fc^+/Fc^0 (Figure 1), which is extremely close to the reduction potential of benzophenone (BP; Figure S1). This feature is assigned to the $\text{C=O/C=O}^{-\bullet}$ couple, which corresponds to the one-electron reduction of the BP group. In contrast, the electrochemical reduction of BP-COOH, a carboxylic acid group attached to the BP structure, is irreversible with a potential of −1.69 V vs. Fc^+/Fc^0. This potential is approximately 0.5 V higher than that of the aforementioned BP-COOMe. Such a large shift may result from the following three possible reasons, including the difference in the electronic effect between COOMe and COOH, the hydrogen-bonding effect, or intramolecular

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Supporting information for this article can be found under:
http://dx.doi.org/10.1002/anie.201607176.

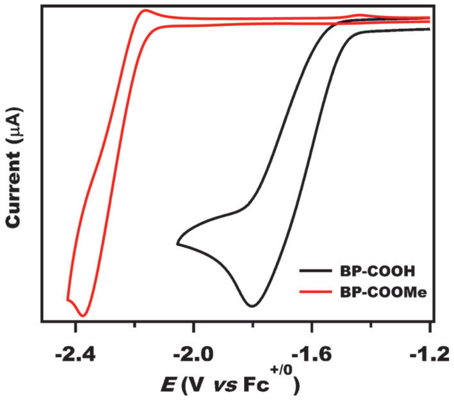


Figure 1. Cyclic voltammograms (CVs) of BP-COOMe (red line) and BP-COOH (black line) in 0.1 M *tetra*-n-butylammonium hexafluorophosphate (TBAF) in degassed acetonitrile. Conditions: glassy carbon electrode as working electrode; Ag^+/Ag as reference electrode; scan rate = 50 $mV s^{-1}$.

proton transfer coupled with electrochemical reduction. The first possibility can be excluded as the electronic effect of COOMe and COOH are almost the same based on their averaged substituent constants (for COOMe: $\sigma_p = 0.45$, $\sigma_m = 0.37$; $\sigma_o = 0.29$; for COOH: $\sigma_p = 0.45$, $\sigma_m = 0.37$; $\sigma_o = 0.23$).[21] If the reduction of BP hydrogen-bonded to an intramolecular carboxylic acid by electron transfer without proton transfer (Scheme S1) is considered to be similar to that occurring in the analysis of the hydrogen-bonded phenols,[12b] the hydrogen-bond strength (below 0.2 eV) is not sufficient to cause such a large potential shift.[12b] The difference of 0.5 V is thus primarily due to the proton transfer from the carboxyl group (COOH) to the BP radical anion. The pK_a value of the benzhydrol radical is around 25 in acetonitrile,[22] which is significantly less acidic than a typical protonated carbonyl group ($pK_a = 0.1$ in CH_3CN)[23] and BP-COOH has a pK_a of around 20 in acetonitrile resulting in a ΔpK_a value of 5 units.[24] The resulting potential shift is close to the observed 0.5 V difference between BP-COOMe and BP-COOH (Scheme S1).

It is well known that cleavage of C–H bonds by benzophenone can occur via its triplet excited electronic state, namely by directly hydrogen-atom transfer or charge transfer followed by proton transfer. Here, kinetic experiments using laser flash photolysis (Figure 2) were performed.

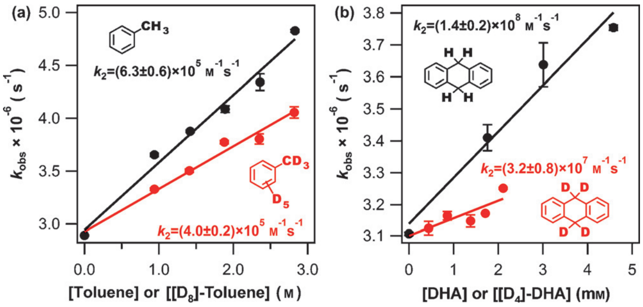


Figure 2. Kinetic study of the reaction of ^{3}*BP-COOMe in the absence or presence of substrates: a) plots of k_{obs} versus [toluene] or [[D$_8$]toluene]; b) plots of k_{obs} versus [DHA] or [[D$_4$]DHA].

In a typical experiment, excitation of a carefully degassed solution of BP-COOR (R = Me or H, 2–3 mM) and DHA (0–3 mM) in acetonitrile under an Ar atmosphere with a 5 ns, 355 nm laser pulse gave the corresponding triplet state (^{3}*BP-COOR). This was evidenced by the rapid appearance of ^{3}*BP-COOR absorption at 530 nm (Figure S3a, S3b). The subsequent bimolecular hydrogen atom transfer reaction between ^{3}*BP-COOR and C–H was monitored by detecting the decay of the ^{3}*BP-COOR absorption at 530 nm (Figure S3d, S3f).

The rate of decay (k_{obs}) of triplet excited electronic states of ketones (^{3*}BP-COOR) is linearly dependent on the concentration of toluene or DHA, thus indicating a bimolecular reaction between triplet ^{3}*BP-COOR and hydrocarbon compounds. The kinetics of these bimolecular reactions obey the equation below (Figure 2 and Figure 3):

$$k_{obs} = k_0 + k_2[\mathrm{C{-}H}] \tag{1}$$

where k_0 is the excited-state-decay rate constants in the absence of substrates (e.g., toluene etc.) and k_2 is the second-order rate constant for the reaction of the excited triplet state (^{3}*BP-COOR) with hydrocarbon substrates. For the reaction between ^{3}*BP-COOR and DHA, ^{3}*BP-COOH is four times faster than ^{3}*BP-COOCH$_3$. This significant difference is likely caused by the introduced Brønsted acid, as it has a similar effect on the reduction potential of the ground state as discussed above, despite there being almost no difference in the electronic effect between -COOCH$_3$ and -COOH.

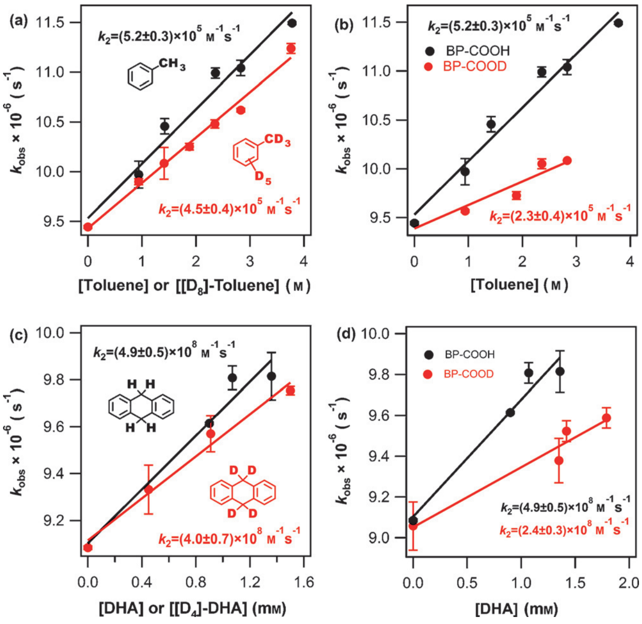


Figure 3. Kinetic study on the reaction of ^{3}*BP-COOH (a, c) and ^{3}*BP-COOD (b, d) with C–H/C–D substrates. a) Plots of k_{obs} versus [toluene] or [[D$_8$]toluene] for the reaction with ^{3}*BP-COOH; b) plots of k_{obs} versus [toluene] for the reactions with ^{3}*BP-COOH and ^{3}*BP-COOD, respectively; c) plots of k_{obs} versus [DHA] or [[D$_4$]DHA] for the reaction with ^{3}*BP-COOH; d) k_{obs} versus [DHA] for the reactions with ^{3}*BP-COOH and ^{3}*BP-COOD, respectively.

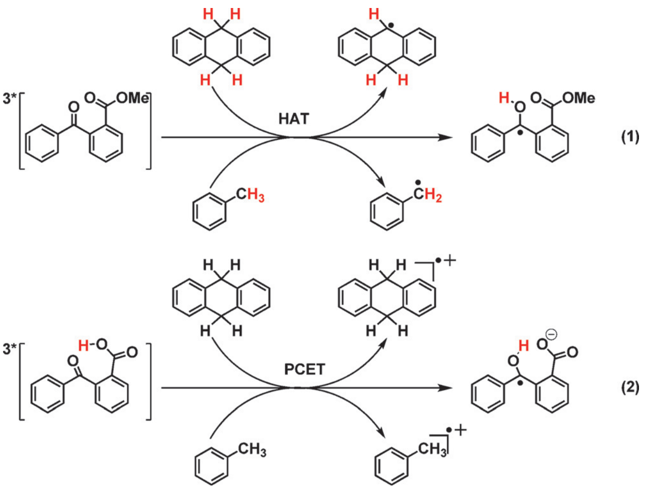
Therefore, the mechanism of hydrocarbon oxidation was investigated to gain insight into how the introduced -COOH group affects the reactivity of the excited state.

The kinetic study was performed for the reaction ^{3}*BP-$COOCH_3$ with $[D_4]$DHA (9, 9, 10, 10-tetradeuteriumanthracene) and $[D_8]$toluene, respectively; which gave $k^{COOMe}_{[D_4]DHA} = 3.2\times10^{7}\,\text{M}^{-1}\,\text{s}^{-1}$, $k^{COOMe}_{[D_8]toluene} = 4.0\times10^{5}\,\text{M}^{-1}\,\text{s}^{-1}$. The C−H/C−D kinetic isotope effect (KIE) values in the case of ^{3}*BP-$COOCH_3$ are 4.4 ± 0.3 and 1.6 ± 0.1 for DHA and toluene, respectively (Figure 2 a, b, Table 1). These values are in accordance with the reported KIE of HAT reactions between ^{3}*BP and hydrocarbons, thus indicating the reaction proceeds by a HAT pathway from hydrocarbon compounds to form ^{3}*BP-$COOCH_3$ [Eq. (1)]. The C−H/C-D kinetic isotope effect (KIE) was repeated for the reaction of ^{3}*BP-COOH with $[D_4]$DHA and $[D_8]$toluene, respectively. Interestingly, the C−H/C−D kinetic isotope effect (KIE) significantly decreased to 1.2 ± 0.2 for DHA and 1.2 ± 0.1 for toluene (Figure 3 c, a, Table 1), thus indicating the reactions might proceed by an alternative pathway that results in a relatively small C−H/C−D KIE and the absence of a HAT from hydrocarbon compounds to ^{3}*BP-COOH.

Table 1: Summary of the KIE data.

	BP-COOMe $KIE_{C-H/C-D}$	BP-COOH $KIE_{C-H/C-D}$	$KIE_{COOH/COOD}$
DHA	4.4 ± 0.3	1.2 ± 0.2	2.1 ± 0.2
Toluene	1.6 ± 0.1	1.2 ± 0.1	2.3 ± 0.2
Benzene	–	–	2.8 ± 0.1

When ^{3}*BP-COOH was the reactant, the C−H/C-D kinetic isotope effect (KIE) decreased. However, the COOH/COOD KIE, for DHA and toluene, was 2.1 ± 0.2 and 2.3 ± 0.2, respectively (Figure 3 d, b, Table 1). These values are comparable with the PCET reactions where the intramolecular carboxylic group acts as a proton donor.[12d] We note that the experiments were performed in acetonitrile, and the pK_a of BP-COOH in acetonitrile is around 20. This significant COOH/COOD KIE indicates a switch in mechanism from a rate-limiting hydrogen atom transfer (HAT) pathway in the case of ^{3}*BP-$COOCH_3$ [Eq. (1)] to a proton-coupled electron-transfer (PCET) pathway in which an electron transfers from the hydrocarbon compounds and the proton is donated by the carboxylic acid group [Eq. (2)]. When compared with the case of ^{3}*BP-$COOCH_3$, the small C−H/C-D KIE (1.2 ± 0.2 for DHA and 1.2 ± 0.1 for toluene) for the case of ^{3}*BP-COOH indicates that the PCET pathway overwhelmingly dominates in the presence of the intramolecular carboxylic acid group [Eq. (2)], otherwise a rate-limiting HAT would be preferred. As described above, the introduced carboxylic acid group likely facilitates the reduction of the carbonyl group in the ground state through proton coupled electron transfer (PCET).



In addition, the oxidation of a series of hydrocarbons (C−H) by the triplet excited electronic states of ^{3}*BP-COOH were also examined under the same conditions as discussed above. There is a very strong correlation between the oxidation rate constants and E_{ox} for the one-electron oxidation of the hydrocarbon compounds (Figure S7a), thus suggesting that all hydrocarbons react with ^{3}*BP-COOH through PCET in which an electron is removed from the hydrocarbons. There is no correlation of the bond dissociation energy (BDE) of hydrocarbons with the oxidation rate constants (Figure S7b), and thus HAT is unlikely to be happened. This is in good agreement with a PCET process that ^{3}*BP-COOH takes one electron from the hydrocarbon substrates and carboxyl group donates a proton [Eq. (2)]; in contrast to hydrogen atom abstraction occurring as in the case of ^{3}*BP-COOMe, this is consistent with the results of the KIE experiments.

The most remarkable effect was showed by the reactions between ^{3}*BP-COOR and benzene (Figure 4). Benzene is difficult to oxidize (3.0 V vs. NHE) and is usually used as an inert solvent. The results show that almost no reaction occurred between ^{3}*BP-COOMe and benzene (red line). In contrast, ^{3}*BP-COOH could oxidize benzene with a second-order rate constant of $8.0\times10^{5}\,\text{M}^{-1}\,\text{s}^{-1}$, and there is a significant primary $KIE_{COOH/COOD} = 2.8 \pm 0.1$. These results indicate that

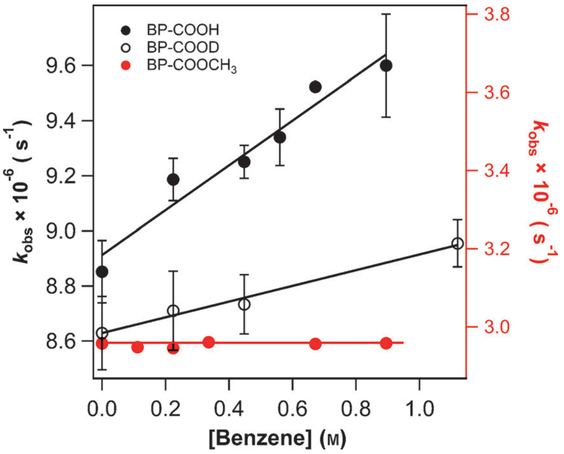


Figure 4. Plots of k_{obs} versus [benzene] for the reactions with ^{3}*BP-COOH (black dot), ^{3}*BP-COOD (black circle), and ^{3}*BP-COOMe (red dot), respectively.

^{3*}BP-COOH could remove one electron from benzene accompanied by a simultaneous proton transfer from the nearby carboxyl group. This is an impressive effect on the reactivity modulation of the excited state by proton-coupled electron transfer.

The reactivity of the organic triplet excited state, ^{3*}BP, has been tuned by utilizing the principle of proton-coupled electron transfer. C–H bond cleavage of toluene derivatives by ^{3*}BP-COOCH$_3$ proceeded by the classic hydrogen-atom transfer (HAT) and exhibited a moderate C–H/C–D KIE (1.8–4). For ^{3*}BP-COOH, the absence of C–H/C–D KIE and a remarkable COOH/COOD KIE result from a switch in the reaction mechanism from direct HAT to concerted electron–proton transfer with the intramolecular -COOH group as proton donor. The PCET oxidation occurs as the ability of ^{3*}BP to remove an electron from the hydrocarbon is significantly increased with the addition of an intramolecular Brønsted acid. Even benzene (ca. 3.0 V vs. NHE) which could not be oxidized by ^{3*}BP-COOMe, could be oxidized by ^{3*}BP-COOH. This simple but effective strategy is of great importance for tuning the reactivity of excited states, which plays a vital role in solar energy conversion and organic photochemistry.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (NSFC Grant No. 21572113), Tsinghua University Initiative Scientific Research Program (Grant No. 20151080404) and National Program for Thousand Young Talents of China. We also acknowledge the instruments platform of CBMS for providing instrumentation.

Keywords: electron transfer · hydrogen-atom transfer · kinetic isotope effect · photochemistry · triplet states

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 13132–13136
Angew. Chem. **2016**, *128*, 13326–13330

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[1] In this paper, HAT indicates the simultaneous transfer of an electron and a proton between the same donor and acceptor, while PCET indicates the simultaneous transfer of an electron and proton between different donors and acceptors; this statement is the same as the generally accepted definition of both HAT and PCET. For more details, please check the following reference: a) S. Hammes-Schiffer, A. A. Stuchebrukhov, *Chem. Rev.* **2010**, *110*, 6939–6960; b) A. Sirjoosingh, S. Hammes-Schiffer, *J. Phys. Chem. A* **2011**, *115*, 2367–2377; c) S. Hammes-Schiffer, *J. Am. Chem. Soc.* **2015**, *137*, 8860–8871.

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Received: July 25, 2016