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# C(sp<sup>3</sup>)–H bond functionalization with styrenes *via* hydrogen-atom transfer to an aqueous hydroxyl radical under photocatalysis<sup>†</sup>

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The redox-neutral addition of  $\alpha$ -C-H bonds of acetonitrile and acetone to styrenes was enabled *via* the hydrogen-atom transfer from relatively acidic and water-miscible C(sp<sup>3</sup>)-H bonds to an aqueous hydroxyl radical generated cleanly and iteratively by the oxidation of water under silver-nanoparticle-loaded titania photocatalysis without using stoichiometric oxidation agents.

One of the most important and fundamental chemical steps in both thermal and photocatalytic organic synthesis is the simultaneous movement of a proton  $(H^+)$  and an electron; this process is known as hydrogen-atom transfer (HAT).<sup>1</sup> Molecular photoredox HAT catalysis has emerged as a powerful strategy for the discovery and development of numerous unique and valuable transformations under mild reaction conditions through open-shell pathways.<sup>2,3</sup> Most of those reported to date involve the cleavage of hydridic to neutral  $C(sp^3)$ -H bonds with electrophilic HAT catalysts generated by the photoexcitation of [Bu<sub>4</sub>N]<sub>4</sub>[W<sub>10</sub>O<sub>32</sub>] (TBADT),<sup>4</sup> aromatic ketones,<sup>5</sup> or the oxidation of organocatalysts using appropriate photoredox catalysts.<sup>2,3</sup> Despite these substantial advancements, HAT from acidic  $\alpha$ -C(sp<sup>3</sup>)-H bonds adjacent to an electron-withdrawing group, such as a cyano or acetyl group, under light still remains elusive (Fig. 1a), probably due to the mismatched polarity and kinetically disfavored transition state; in fact, the  $\beta$ -C(sp<sup>3</sup>)-H bonds of alkylnitriles and alkylketones are more smoothly functionalized by well-established electrophilic HAT catalysts than  $\alpha$ -C(sp<sup>3</sup>)-H bonds.<sup>6,7</sup> The removal of this obstacle would pave the way for new radical chemistry that would diversify organic synthesis.8-14 Very recently, photocatalytic HAT was demonstrated to occur from acidic C(sp<sup>3</sup>)-H bonds to aryl radicals (Ar<sup>•</sup>)<sup>15–17</sup> or oxygen-centered carboxy radicals (RCOO<sup>•</sup>)<sup>18</sup> (Fig. 1b). The thermodynamic driving force for

the cleavage of the relatively polarized and acidic  $C(sp^3)$ -H bonds is the formation of strong Ar-H (BDE  $\approx 113$  kcal mol<sup>-1</sup>) and RCOO-H (C<sub>6</sub>H<sub>5</sub>COO-H, BDE = 105 kcal mol<sup>-1</sup>) bonds, which offsets the difficulty of the homolytic cleavage of NCCH<sub>2</sub>-H (pK<sub>a</sub> = 31 in DMSO; BDE = 93 kcal mol<sup>-1</sup>) and CH<sub>3</sub>COCH<sub>2</sub>-H (pK<sub>a</sub> = 27 in DMSO; BDE = 95 kcal mol<sup>-1</sup>) bonds.<sup>19-23</sup> However, in these strategies, the Ar', RCOO', or other radical species<sup>24-26</sup> were used as sacrificial agents. Therefore, the development of a straightforward catalytic method to avoid the generation of stoichiometric organic and/ or inorganic waste remains a significant challenge.

Herein, we report that the  $\alpha$ -C-H bonds of acetonitrile (CH<sub>3</sub>CN, **2a**) and acetone [(CH<sub>3</sub>)<sub>2</sub>CO, **2b**] can, despite their relatively high acidity, undergo addition to the C=C double bonds



This work

c) Radicals via atom-efficient HAT from C(sp<sup>3</sup>)-H in water



Fig. 1 Inspiration for the development for the hydrogen-atom transfer (HAT) from acidic  $C(sp^3)$ -H bonds.

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of styrenes *via* HAT from the  $\alpha$ -C–H bonds to a hydroxyl radical ('OH) generated using Ag/TiO<sub>2</sub> and water under LED irradiation ( $\lambda$  = 365 nm) without generating stoichiometric waste (Fig. 1c). While the generation of the  $\alpha$ -carbon-centered radicals of **2a** and **2b** catalyzed by the photo-generated, electrophilic OH radical in water ['OH…(H<sub>2</sub>O)<sub>n</sub>: 'OH randomly delocalized in bulk water] is kinetically relatively unfavorable, it is thermodynamically more favorable, as the major driving force of the reaction is the formation of an extremely strong HO-H bond (BDE = 119 kcal mol<sup>-1</sup>).<sup>20,21,27,28</sup> Although there have been several reports of oxidative reactions of olefins *via* the addition of 'CH<sub>2</sub>CN or 'CH<sub>2</sub>COCH<sub>3</sub>,<sup>8-12,15,16,18,24</sup> examples for an overall redox-efficient catalysis remains scarce.<sup>29,30</sup> The reactions using 'CH<sub>2</sub>CN under Pd/TiO<sub>2</sub> or Pt/TiO<sub>2</sub> photocataly-sis has been reported, albeit that the productivity was low.<sup>31-33</sup>

The semiconductor photocatalyst TiO<sub>2</sub> is photostable, thermally stable, and tolerant of radicals and anionic nucleophiles, which often degrade other catalysts. TiO2 has a bandgap suitable for the oxidation and reduction of many cheap, practical, and stable chemicals, especially the oxidation of water to 'OH.<sup>34,35</sup> The OH radicals easily undergo hydrogen abstraction from, and addition to, organic frameworks, which have been used extensively for the so-called 'cold combustion' of organic waste/contaminants through their degradation to CO2.36-38 In contrast, transformations involving the controlled cleavage and formation of chemical bonds mediated by 'OH are scarce, and those that have been reported are impractical in terms of productivity and selectivity.<sup>39</sup> In other words, the use of 'OH for selective organic synthesis has so far been far beyond the scope of existing catalytic approaches. Considering the higher reactivity of 'OH in HAT in water than in organic solvents,<sup>40</sup> and the undesired addition of 'OH to aromatic compounds,<sup>41,42</sup> we envisioned that the selective HAT from highly water-miscible C-H bonds to 'OH in the aqueous phase favorably occurs against decomposition of poorly water-miscible styrenes and the coupling products, both being favorably deployed in the organic phase. With the aim of making such a ground-breaking achievement based on our continuous development of the semiconductor-based photocatalysis of alcohols for practical and selective N-alkylation reactions,43-45 we screened various metal nanoparticle-loaded TiO<sub>2</sub> (M/TiO<sub>2</sub>) materials for their ability to functionalize relatively acidic  $\alpha$ -C-H bonds in a water-based photocatalytic system.

Initially, a series of reactions using  $\alpha$ -methyl styrene (**1a**) was carried out using an aqueous mixture of **2a** and the photocatalyst under LED-light irradiation ( $\lambda$  = 365 nm) and N<sub>2</sub> at ambient temperature to optimize the reaction conditions (Table 1), since, unlike aliphatic alkenes, styrenes were poor coupling partners in relevant radical chain reactions, in which a stoichiometric oxidant is even needed.<sup>30</sup> The metal (M) loading of TiO<sub>2</sub> was found to be critical for the effective addition of **2a** to **1a**. Among the various M/TiO<sub>2</sub> combinations tested, only Ag (5 wt%)/TiO<sub>2</sub> gave the desired product (**3aa**) in acceptable yield (69%; Table 1, entry 3); the efficiency of the product formation using pristine TiO<sub>2</sub> (P25) and other M/TiO<sub>2</sub> catalysts was rela-

 $\label{eq:table_$ 

+ H CN 1a, 0.2 mmol 2a, 1 mL	Ag(1 wt%)/TiO <sub>2</sub> (10.0 mg) H <sub>2</sub> O (1 mL) KOH (0.02 mmol) <i>hν</i> (365 nm), r.t., N <sub>2</sub> , 24 h	CN 3aa
Entry Photocatalyst	Changes from standard conditions	Yield <sup>b</sup> (%)
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	$\begin{array}{ccc} &\\ & -\\ & -\\ & -\\ & -\\ & -\\ & -\\ & $	$ \begin{array}{c} -c \\ \leq 20 \\ 69 \\ 86 (85) \\ -c \\ 15 \\ -c \\ \end{array} $

<sup>*a*</sup> Standard conditions: **1a** (0.2 mmol), **2a** (1 mL, 19.0 mmol), Ag (1 wt%)/TiO<sub>2</sub> (10.0 mg), H<sub>2</sub>O (1 mL), and KOH (0.02 mmol) in the presence of LED light ( $\lambda$  = 365 nm) at room temperature under N<sub>2</sub> for 24 h. <sup>*b*</sup> <sup>1</sup>H NMR yield of **3aa**. Isolated yield in parentheses. <sup>*c*</sup> Not detected. <sup>*d*</sup> M = Co, Ni, Cu, Rh, Pd, Ir, Pt, or Au. <sup>*e*</sup> Dehydrated **2a** (2 mL) was used. <sup>*f*</sup> 4-Hydroxy-4-phenylpentanenitrile (**3aa**', 16%) was isolated (Scheme S1†). See ESI† for experimental details.

tively poor ( $\leq 20\%$ ; Table 1 entries 1 and 2; Table S1<sup>†</sup>). The loading of noble transition metals, including Ag, on TiO<sub>2</sub> can facilitate charge [hole (h<sup>+</sup>) and electron (e)] separation and effectively prevent h<sup>+</sup>/e recombination.<sup>46</sup> Unlike other noble metal M/TiO<sub>2</sub> catalysts, hydrogen atoms generated via the reduction of H<sup>+</sup> on the metal nanoparticles do not readily recombine to give dihydrogen over Ag/TiO<sub>2</sub> (Table S1<sup>†</sup>).<sup>43,46</sup> In addition, pristine TiO<sub>2</sub> cannot resupply a hydrogen atom to the benzylic radical, which may be an intermediate formed by the addition of 'CH<sub>2</sub>CN to **1a**.<sup>47</sup> These facts may partially account for the efficiency of Ag/TiO<sub>2</sub> in this transformation. The yield of 3aa was further improved by reducing the loading of Ag on  $TiO_2$ , and the exclusive formation of 3aa was observed with Ag (1 wt%)/TiO<sub>2</sub> (85% isolated yield; Table 1 entry 4; Table S2<sup>†</sup>). The turnover number (TON: mol/mol) based on Ag is 204. Photosensitized TBADT or benzophenone used in place of Ag/ TiO<sub>2</sub> under otherwise identical reaction conditions failed to catalyze this transformation (Table S3<sup>†</sup>).<sup>4,5</sup> Although a base additive was not required to achieve the coupling (Table 1 entry 7), the addition of KOH (10 mol%) significantly accelerated the reaction, leading to superb reactivity (Table S4<sup>†</sup>). Control experiments verified the necessity of Ag(1 wt%)/TiO2, LED-light irradiation, KOH, water, and an N2 atmosphere for an efficient transformation (Table 1, entries 5-10). Gratifyingly, the desired reaction occurred effectively using the optimal, standard conditions (Table 1, footnote a).

With the standard conditions in hand, we examined the substrate scope with respect to the styrene component (Table 2). A scalable production of **3ba** from a 1 mmol of **1b** was also successful (Scheme S2<sup>†</sup>). Both electron-deficient and electron-rich  $\alpha$ -methyl styrenes underwent the reaction (**3ba**:





<sup>*a*</sup> Isolated yield. Using **1** (0.2 mmol), **2** (1 mL), Ag(1 wt%)/TiO<sub>2</sub> (10.0 mg), H<sub>2</sub>O (1 mL), and KOH (0.02 mmol) in the presence of LED light ( $\lambda$  = 365 nm) at room temperature under N<sub>2</sub> for 24 h. <sup>*b*</sup> Used **1b** (1 mmol). <sup>*c*</sup> Ag(1 wt%)/TiO<sub>2</sub> (20.0 mg). <sup>*d*</sup> **1** (0.1 mmol), Ag(1 wt%)/TiO<sub>2</sub> (20.0 mg). <sup>*e*</sup> Ag (1 wt%)/TiO<sub>2</sub> (50.0 mg). See ESI<sup>+</sup> for experimental details.

92%; **3ca**: 83%; **3da–3fa**: 64–84%). An *ortho*-substituent (**3ga**: 44%), the halogens F and Cl (**3ha** and **3ia**: ~70%), and pyridines (**3ja–3la**: 50–74%) were well tolerated. Styrenes that do not bear an  $\alpha$ -methyl group also afforded the desired products (**3ma–3qa**: 68–87%), suggesting that the transient stabilization of benzylic radicals by substitution is not mandatory. Likewise, **2b** underwent addition of its  $\alpha$ -carbon to a wide variety of styrenes (**3ab**, **3bb**, **3db**, **3gb**, **3mb** and **3qb**: up to 96%).

Versatile commodity organic solvents were also tested as coupling partners for styrenes (Table 3). Highly water-miscible solvents such as THF (**2c**), **1**,4-dioxane (**2d**), DMF (**2e**), and DMA (**2f**) gave the desired C–C coupling products in good to excellent yield. Even the  $\alpha$ -carbon of the unactivated amide DMA was slightly alkylated. Surprisingly, C–C coupling of 4-methylstyrene (**1m**) did not take place with poorly water-miscible **2g–2j**, which are structurally analogous to **2a–2d**, nor did the reaction proceeded with **2k**, which has a neutral and relatively weak C(sp<sup>3</sup>)–H bond (p $K_a$  = 43 in DMSO; BDE = 90 kcal mol<sup>-1</sup>).<sup>19,22</sup> Oil/water-biphasic mixtures were readily formed with **2g–2k**, suggesting that the formation and reaction of 'OH are only viable in water,<sup>40,48</sup> as the Ag/TiO<sub>2</sub> is present in the aqueous phase (Table S5†).

To gain further insight into the catalytic cycle, control experiments were carried out (Fig. 2). First, the formation of 'OH in the presence of irradiated Ag(1 wt%)/TiO2 in water was confirmed by the fluorescence change when the aqueous 'OH was trapped by water-miscible coumarin (Fig. S2<sup>†</sup>).<sup>49</sup> Secondly, the radical scavenger (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO; 4 equiv. relative to 1a) was added to a 2a/H2O-KOH system under the standard conditions (irradiation time: 6 h) (Fig. 2a; Table S6<sup>†</sup>). As a result, the C-C coupling step was significantly inhibited; instead, 5a was obtained as a result of the coupling of 'CH<sub>2</sub>CN with TEMPO, which is not miscible with water (the water phase was not colored red by TEMPO). These results suggest a possibility of a free radical coupling process at the interface of the water and organic phase ('on water').50 A similar result was obtained using the 2b/H2O-KOH system (Table S7†). Thirdly, deuterium (D)-labelling experiments were performed under the standard conditions. When previously synthesized 3aa was added to  $2a \cdot d_3/D_2O$ -KOH and irradiated, H-D exchange barely occurred at the benzylic position or  $\alpha$ -position of 3aa, suggesting that 3aa effectively escaped from the aqueous phase containing HO<sup>-</sup> and 'OH after its formation (Fig. 2b, eqn (1); Fig. S3<sup>†</sup>), whereas D was







incorporated exclusively at the benzylic position during the reaction of 1a in  $2a-d_3/D_2O$ -KOH (Fig. 2b, eqn (2); Fig. S4<sup>†</sup>). In sharp contrast, D-incorporation at the same carbon atom scarcely occurred when 1a was reacted in  $2a - d_3/H_2O$ -KOH (Fig. 2b, eqn (3); Fig. S5<sup> $\dagger$ </sup>). These results suggest that H<sub>2</sub>O is the exclusive source of the hydrogen atoms (H<sup>•</sup>) supplied to the benzylic radicals in the system; H' is generated upon the reduction of H<sup>+</sup> by e on Ag and stabilized by the Ag/TiO<sub>2</sub> surface.<sup>43</sup> In the reaction of 1a in 2a/D2O-KOH, D was not incorporated at the  $\alpha$ -position of the cyano group, while the benzylic position was almost fully deuterated, suggesting that H-D exchange between 2a and  $D_2O$  was so sluggish that the nitrile enolate is hardly formed to participate in the coupling (Fig. 2b, eqn (4); Fig. S6†). The deuteration frequency was easily altered, selectively furnishing  $3aa-d_1$ ,  $3aa-d_2$ , and  $3aa-d_3$ . An experiment using a 1:1 (v/v) mixture of 2a and 2a- $d_3$  with H<sub>2</sub>O under the standard coupling conditions gave a mixture of 3aa and 3aa- $d_2$ with a large kinetic isotope effect ( $k_{\rm H}/k_{\rm D}$  = 8.9), indicating that the cleavage of the  $\alpha$ -C(sp<sup>3</sup>)-H bond of 2a would be the ratedetermining step (Fig. 2b, eqn (5); Fig. S7<sup>†</sup>). Such a large  $k_{\rm H}/k_{\rm D}$ (>7) would imply that the HAT reaction resulted from the quantum mechanical tunnelling.51 Similar trends were observed in the coupling of 2b, although the more acidic and water-mis-





**Fig. 2** (a) Radical-trapping experiments. <sup>1</sup>H NMR yields of **3aa** and **5a**. (b) Labelling experiments. Conversion of **1a** determined by GC-MS analysis. Isolated yields of **3aa**, **3aa**- $d_3$ , **3aa**- $d_2$ , and **3aa**- $d_1$ . D/H ratio determined by <sup>1</sup>H NMR analysis of the isolated products. (c) Plausible mechanism. h<sup>+</sup> = hole, e = electron, CB = conduction band, VB = valence band. See ESI† for experimental details.

cible  $\alpha$ -C-H bonds of **2b**, **2b**-*d*<sub>6</sub>, and **3ab** underwent feasible H– D scrambling with D<sub>2</sub>O or H<sub>2</sub>O (Fig. S8–11†).

Based on the experimental data, and interpretations in preceding reports that the radical chain propagation *via* HAT to benzylic radicals from substrate C-H bonds is energetically **Table 4**Comparison of green chemistry metrics for the addition of<br/>acetonitrile or acetone to alkenes using different protocols

Entry	1	2	3	4
Reference number AE $(\%)^a$ RME $(\%)^b$ PMI (reaction) <sup>c</sup> PMI (reactant, reagent, catalyst) <sup>c</sup> TON <sup>d</sup>	This work 100 7.7 29 13 171 <sup>e</sup>	29 100 1.4 70 70	$30 \\ 100 \\ 1.2 \\ 86 \\ 86 \\ 9^{f}$	$25 \\ 100 \\ 0.9 \\ 121 \\ 121 \\ 2^{g}$

<sup>*a*</sup> Atom economy. <sup>*b*</sup> Reaction mass efficiency. <sup>*c*</sup> Process mass intensity. <sup>*d*</sup> Turnover number (mol/mol). <sup>*e*</sup> Based on Ag. <sup>*f*</sup> Based on CuI. <sup>*g*</sup> Based on 4,4'-dichlorobenzophenone. See ESI (page S33†) for the reactions and calculation details.

unfavourable,<sup>21,30,47</sup> a plausible redox-neutral mechanism is proposed (Fig. 2c). Upon photoexcitation, Ag/TiO<sub>2</sub> generates excited e and h<sup>+</sup> pairs. Considering that water, rather than KOH, plays a crucial role in the success of the coupling (Table 1 entries 7-9; Table S8<sup>†</sup>), as well as the well-known strong hydrophilicity of the TiO<sub>2</sub> surface,<sup>52</sup> H<sub>2</sub>O can be expected to be initially oxidized to  $(H_2O)_n$  by h<sup>+</sup> on/near the TiO<sub>2</sub> surface.<sup>34,35</sup> Thereafter, hydrogen abstraction directly from 2a by 'OH, which gives H<sub>2</sub>O and 'CH<sub>2</sub>CN, would be more plausible than other pathways including oxidation of enolate species.<sup>53,54</sup> After the addition of 'CH<sub>2</sub>CN to the C=C double bond of styrenes, the formation of benzylic radicals would be followed by coupling with an H<sub>2</sub>Oderived H on Ag/TiO<sub>2</sub> (the photo-excited e and H<sup>+</sup> split from water) to give the final coupling products, which are poorly water-miscible and are thus effectively expelled from the catalytic cycle, the majority of which occurs in water-miscible phase.

Green chemistry metrics of the present carbon–carbon bond forming reaction prevails over that of a couple of relevant reactions previously reported (Table 4). $^{55}$ 

# Conclusions

To summarize, emphasis should be placed on the characteristics of the current novel results, in which a water-solvated 'OH ['OH…(H<sub>2</sub>O)<sub>*n*</sub>] is cleanly and iteratively generated from H<sub>2</sub>O and it promotes a selective HAT reaction. The anomalous restoration/ recycling feature of H<sub>2</sub>O/'OH stands in marked contrast to the unidirectional formation of 'OH *via* the thermal decay of hydrogen peroxide, *e.g.*, using the Fenton reagent,<sup>56,57</sup> as a stoichiometric agent. Another important aspect of our system is the use of water as the solvent, which prevents poorly water-miscible organic components from undergoing undesirable hydrogen abstraction by 'OH or addition of 'OH, which often leads to complex contamination attributable to undesired side reactions.

# Author contributions

The manuscript consists of contributions from all authors. All authors have given approval to the final version of the manuscript.

### Conflicts of interest

There are no conflicts to declare.

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#### References

- 1 S. Hammes-Schiffer, *Energy Environ. Sci.*, 2012, 5, 7696–7703.
- 2 L. Capaldo and D. Ravelli, Eur. J. Org. Chem., 2017, 2056–2071.
- 3 L. Capaldo, L. L. Quadri and D. Ravelli, *Green Chem.*, 2020, 22, 3376–3396.
- 4 D. Ravelli, M. Fagnoni, T. Fukuyama, T. Nishikawa and I. Ryu, *ACS Catal.*, 2018, **8**, 701–713.
- 5 C. Chen, Org. Biomol. Chem., 2016, 14, 8641-8647.
- 6 K. Yamada, M. Okada, T. Fukuyama, D. Ravelli, M. Fagnoni and I. Ryu, *Org. Lett.*, 2015, **17**, 1292–1295.
- 7 M. Okada, T. Fukuyama, K. Yamada, I. Ryu, D. Ravelli and M. Fagnoni, *Chem. Sci.*, 2014, **5**, 2893–2898.
- 8 X.-Q. Chu, D. Ge, Z.-L. Shen and T.-P. Loh, ACS Catal., 2018, 8, 258–271.
- 9 R. Zhang, S. Jin, Q. Liu, S. Lin and Z. Yan, *J. Org. Chem.*, 2018, **83**, 13030–13035.
- 10 C. Xu, Y. Han, S. Chen, D. Xu, B. Zhang, Z. Shan, S. Du, L. Xu and P. Gong, *Tetrahedron Lett.*, 2018, **59**, 260– 263.
- 11 X.-W. Lan, N.-X. Wang, W. Zhang, J.-L. Wen, C.-B. Bai, Y. Xing and Y.-H. Li, *Org. Lett.*, 2015, **17**, 4460–4463.
- 12 D. Liang, X. Song, L. Xu, Y. Sun, Y. Dong, B. Wang and W. Li, *Tetrahedron*, 2019, 75, 3495–3503.
- 13 G. Hong, P. D. Nahide and M. C. Kozlowski, *Org. Lett.*, 2020, 22, 1563–1568.
- 14 Y. Xiao and Z.-Q. Liu, Org. Lett., 2019, 21, 8810-8813.
- 15 M. Anselmo, A. Basso, S. Protti and D. Ravelli, *ACS Catal.*, 2019, **9**, 2493–2500.
- 16 J.-L. Zhang, Y. Liu, R.-J. Song, G.-F. Jiang and J.-H. Li, *Synlett*, 2014, **25**, 1031–1035.
- 17 J. Kang, H. S. Hwang, V. K. Soni and E. J. Cho, *Org. Lett.*, 2020, 22, 6112–6116.
- 18 J. Fang, W.-L. Dong, G.-Q. Xu and P.-F. Xu, Org. Lett., 2019, 21, 4480–4485.
- 19 X.-S. Xue, P. Ji, B. Zhou and J.-P. Cheng, *Chem. Rev.*, 2017, 117, 8622–8648.
- 20 J. A. Kerr, Chem. Rev., 1966, 66, 465-500.
- 21 Y.-R. Luo, Handbook of Bond Dissociation Energies in Organic Compounds, CRC Press, Boca Raton, 2002.
- 22 F. G. Bordwell, Acc. Chem. Res., 1988, 21, 456-463.

- 23 H.-G. Korth and W. Sicking, J. Chem. Soc., Perkin Trans. 2, 1997, 715–719.
- 24 Q.-L. Wang, Z. Chen, C.-S. Zhou, B.-Q. Xiong, P.-L. Zhang, C.-A. Yang, Y. Liu and Q. Zhou, *Tetrahedron Lett.*, 2018, 59, 4551–4556.
- 25 T. Yamashita, M. Watanabe, R. Kojima, T. Shiragami,
  K. Shima and M. Yasuda, *J. Photochem. Photobiol.*, A, 1998,
  118, 165–171.
- 26 T. Yamashita, M. Yasuda, M. Watanabe, R. Kojima, K. Tanabe and K. Shima, *J. Org. Chem.*, 1996, 61, 6438–6441.
- 27 H. Marusawa, K. Ichikawa, N. Narita, H. Murakami, K. Ito and T. Tezuka, *Bioorg. Med. Chem.*, 2002, **10**, 2283–2290.
- 28 F. D. Vleeschouwer, V. V. Speybroeck, M. Waroquier, P. Geerlings and F. D. Proft, *Org. Lett.*, 2007, 9, 2721–2724.
- 29 T. Kamitanaka, T. Hikida, S. Hayashi, N. Kishida, T. Matsuda and T. Harada, *Tetrahedron Lett.*, 2007, **48**, 8460-8463.
- 30 Z. Li, Y. Xiao and Z.-Q. Liu, *Chem. Commun.*, 2015, **51**, 9969–9971.
- 31 H. Yoshida, Y. Fujimura, H. Yuzawa, J. Kumagai and T. Yoshida, *Chem. Commun.*, 2013, 49, 3793–3795.
- 32 E. Wada, T. Takeuchi, Y. Fujimura, A. Tyagi, T. Kato and H. Yoshida, *Catal. Sci. Technol.*, 2017, 7, 2457–2466.
- 33 Y. Fan, S. Li, J. Bao, L. Shi, Y. Yang, F. Yu, P. Gao, H. Wang,
   L. Zhong and Y. Sun, *Green Chem.*, 2018, 20, 3450–3456.
- 34 W. Kim, T. Tachikawa, G. Moon, T. Majima and W. Choi, Angew. Chem., Int. Ed., 2014, 53, 14036–14041.
- 35 Y. Nosaka and A. Nosaka, ACS Energy Lett., 2016, 1, 356–359.
- 36 M. R. Hoffmann, S. T. Martin, W. Choi and D. W. Bahnemann, *Chem. Rev.*, 1995, **95**, 69–96.
- 37 K. S. Varma, R. J. Tayade, K. J. Shah, P. A. Joshi, A. D. Shukla and V. G. Gandhi, *Water-Energy Nexus*, 2020, 3, 46–61.
- 38 D. Chen, Y. Cheng, N. Zhou, P. Chen, Y. Wang, K. Li,
  S. Huo, P. Cheng, P. Peng, R. Zhang, L. Wang, H. Liu,
  Y. Liu and R. Ruan, *J. Cleaner Prod.*, 2020, 268, 121725.
- 39 Y. Wang, A. Liu, D. Ma, S. Li, C. Lu, T. Li and C. Chen, *Catalysts*, 2018, **8**, 355.

- 40 S. Mitroka, S. Zimmeck, D. Troya and J. M. Tanko, J. Am. Chem. Soc., 2010, **132**, 2907–2913.
- 41 M. P. DeMatteo, J. S. Poole, X. Shi, R. Sachdeva, P. G. Hatcher, C. M. Hadad and M. S. Platz, *J. Am. Chem. Soc.*, 2005, **127**, 7094–7109.
- 42 J. S. Poole, X. Shi, C. M. Hadad and M. S. Platz, *J. Phys. Chem. A*, 2005, **109**, 2547–2551.
- 43 V. N. Tsarev, Y. Morioka, J. Caner, Q. Wang, R. Ushimaru, A. Kudo, H. Naka and S. Saito, *Org. Lett.*, 2015, **17**, 2530– 2533.
- 44 L.-M. Wang, K. Jenkinson, A. E. H. Wheatley, K. Kuwata, S. Saito and H. Naka, ACS Sustainable Chem. Eng., 2018, 6, 15419–15424.
- 45 L.-M. Wang, Y. Morioka, K. Jenkinson, A. E. H. Wheatley, S. Saito and H. Naka, *Sci. Rep.*, 2018, **8**, 6931.
- 46 A. Sclafani, M.-N. Mozzanega and P. Pichat, *J. Photochem. Photobiol.*, *A*, 1991, **59**, 181–189.
- 47 Q. Zhu and D. G. Nocera, *J. Am. Chem. Soc.*, 2020, **142**, 17913–17918.
- 48 Y. Hayashi, Angew. Chem., Int. Ed., 2006, 45, 8103-8104.
- 49 J. Zhang and Y. Nosaka, J. Photochem. Photobiol., A, 2015, 303-304, 53-58.
- 50 S. Narayan, J. Muldoon, M. G. Finn, V. V. Fokin, H. C. Kolb and K. B. Sharpless, *Angew. Chem., Int. Ed.*, 2005, 44, 3275– 3279.
- 51 J. Meisner and J. Kästner, *Angew. Chem., Int. Ed.*, 2016, 55, 5400–5413.
- 52 R. Wang, K. Hashimoto, A. Fujishima, M. Chikuni, E. Kojima, A. Kitamura, M. Shimohigoshi and T. Watanabe, *Nature*, 1997, **388**, 431–432.
- 53 F. Wang, X. Zhang, Y. He and X. Fan, *J. Org. Chem.*, 2020, **85**, 2220–2230.
- 54 S. Baś, Y. Yamashita and S. Kobayashi, ACS Catal., 2020, 10, 10546–10550.
- 55 C. R. McElroy, A. Constantinou, L. C. Jones, L. Summerton and J. H. Clark, *Green Chem.*, 2015, **17**, 3111–3121.
- 56 C. Walling, Acc. Chem. Res., 1975, 8, 125-131.
- 57 C. L. Keller, J. D. Dalessandro, R. P. Hotz and A. R. Pinhas, J. Org. Chem., 2008, 73, 3616–3618.