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ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY B · AUGUST 2014

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# Investigation of the Role of Protonation of Benzophenone and Its Derivatives in Acidic Aqueous Solutions Using Time-Resolved Resonance Raman Spectroscopy: How Are Ketyl Radicals Formed in Aqueous Solutions?

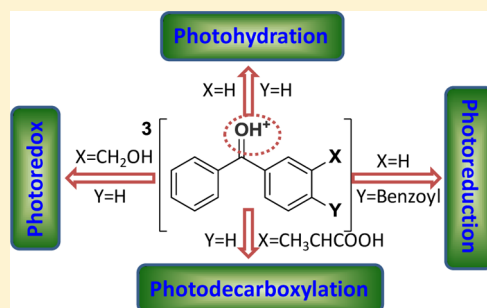
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## Supporting Information

**ABSTRACT:** The formation mechanism of ketyl radicals and several other selective photoreactions of benzophenone and its derivatives are initiated by the protonation of their triplet state and have been investigated using nanosecond time-resolved resonance Raman spectroscopy (ns-TR<sup>3</sup>) in solutions of varying conditions. Evidence is found that the ketyl radical is generated by the combined action of a ketone protonation and a subsequent electron transfer based on the results from previous studies on the photochemistry and photophysics of benzophenone and the ns-TR<sup>3</sup> results reported here for benzophenone, 1,4-dibenzoylbenzene, 3-(hydroxymethyl)-benzophenone, and ketoprofen in neutral and acidic solution. In order to better understand the role of the protonated ketone, results are summarized for some selective photochemical reactions of benzophenone and its derivatives induced by protonation in acidic solutions. For the parent benzophenone, the protonation of the ketone leads to the photohydration reactions at the ortho- and meta-positions of the benzene ring in acidic aqueous solutions. For 3-(hydroxymethyl)benzophenone, the protonation promotes an interesting photoredox reaction to become very efficient and the predominant reaction in a pH = 2 aqueous solution. While for ketoprofen, the protonation can initiate a solvent-mediated excited-state intramolecular proton transfer (ESIPT) from the carboxyl group to the carbonyl group that then leads to a decarboxylation reaction in a pH = 0 acidic aqueous solution. We briefly discuss the key role of the protonation of the ketone in the photochemistry of these aromatic ketones.



## INTRODUCTION

The photophysics and photochemistry of benzophenone (BP) has been intensely investigated, since it is a benchmark aromatic ketone.<sup>1–10</sup> The small energy gap, and the strong spin–orbit coupling between BP's lowest excited singlet state ( $S_1$   $n,\pi^*$ ) and its second excited triplet state ( $T_2$   $\pi,\pi^*$ ) enable an intersystem crossing (ISC) process to compete very effectively with other  $S_1$  state processes like internal conversion (IC) and fluorescence emission so that the  $T_1$  state is produced with a large yield close to unity.<sup>11,12</sup> Therefore, the lowest excited triplet ( $T_1$   $n,\pi^*$ ) is responsible for most of the subsequent photochemical processes and reactions in the solution phase.<sup>11,12</sup> For example, the  $T_1$  state of BP can undergo a hydrogen abstraction reaction with hydrogen donors to produce a diphenyl ketyl (DPK) radical that can then react with the other radical species like those formed from the reaction with the H-donor solvent to generate long-lived light-absorbing transients (LAT).<sup>13–15</sup> Although there have been many studies done for the BP photoreduction reaction mechanism performed in a variety of organic solvents, only a few studies have examined the corresponding photochemical and photophysical processes in water which is considered to be

a relatively “inert” hydrogen-donor solvent. Ledger and Porter first reported that the phosphorescence of BP in aqueous solution is quenched by protons with a rate constant of  $6 \times 10^8$   $M^{-1} s^{-1}$  and that photolysis of BP in aqueous solution can also generate the DPK radical through a hydrogen abstraction from water by the triplet state of BP ( $^3BP$ ).<sup>16</sup> However, the mechanism remained unclear and there was a lack of information about what caused this quenching and how the DPK radical was formed in an aqueous solution. Since then, several studies have examined the photoinduced processes of BP in aqueous solution.<sup>17–26</sup> Wyatt and co-workers<sup>17,18</sup> investigated the protonation equilibrium of  $^3BP$  by flash photolysis of BP over a wide range of acid concentrations and determined a  $pK_a$  of 1.5 for  $^3BP$ . They found that the lifetime of  $^3BP$  drops below 100 ns around pH = 0, whereas 64

**Special Issue:** Photoinduced Proton Transfer in Chemistry and Biology Symposium

**Received:** June 16, 2014

**Revised:** August 11, 2014

that of its conjugate acid  ${}^3\text{BPH}^+$  rises to 50  $\mu\text{s}$  in degassed solutions with higher acidities, and hence, they concluded “A possible explanation is that water is an effective quencher of  ${}^3\text{BPH}^+$ ”. Despite a number of follow-up studies,<sup>19–21</sup> a satisfactory explanation for this puzzling phenomenon has not come forth. In a recent study, Wirz and co-workers<sup>27</sup> reported that an acid-catalyzed photohydration is responsible for the triplet-quenching process observed in a moderate acidic aqueous solution. In this triplet-quenching process, the initial protonation of carbonyl oxygen in  ${}^3\text{BP}$  produces the corresponding excited triplet state conjugate acid ( ${}^3\text{BPH}^+$ ). Additionally, the positive charge of the protonated species ( ${}^3\text{BPH}^+$ ) may induce significant delocalization at the ortho- and meta-positions of the benzene ring. On the basis of Zimmerman’s ortho–meta effect for the benzene ring site activation in photochemical reactions,<sup>28,29</sup> these two sites having a positive charge can be attacked by the water molecule to produce short-lived hydration intermediates ( $o\text{-}{}^3\text{BP}\cdot\text{H}_2\text{O}$  and  $m\text{-}{}^3\text{BP}\cdot\text{H}_2\text{O}$ ) that subsequently deactivate to the ground state ( $o\text{-}{}^1\text{BP}\cdot\text{H}_2\text{O}$ ) or proceed directly to the parent BP molecule by dehydration reactions.<sup>27</sup> Although a number of groups have conducted many investigations on the photoreduction reaction of  ${}^3\text{BP}$  in neutral and acidic aqueous solution, there are still some gaps that remain to be elucidated. (1) The clear and definitive characterization of the BP transient species’ kinetics and other properties is hampered when using only transient absorption spectroscopy, owing to the overlapping of the broad featureless absorption bands of these species that exist on the same timescale. Therefore, time-resolved vibrational spectroscopy, especially time-resolved resonance Raman spectroscopy, can be particularly useful to characterize the structures and dynamics of the critical intermediates involved in the photochemical reactions of BP and its derivatives in aqueous solution.<sup>30–38</sup> (2) Although a number of studies have claimed that the  ${}^3\text{BP}$  species may give rise to the formation of a DPK radical intermediate in aqueous solution, the mechanism for the formation of the DPK radical remains a matter of uncertainty.<sup>16,34,35</sup> (3) Wirz and co-workers reported that the protonation of  ${}^3\text{BP}$  is responsible for the photohydration reaction. This naturally brings up the question: what is role of the protonation of the ketone for other BP derivatives? In this paper, we will present some new experimental spectra on several BP derivatives in aqueous solutions under various pH conditions that combined with a comparison to previous results in the literature help to better understand the role of the protonation of the BP moiety in BP-containing compounds that enable new types of photochemical reactions to take place in acid aqueous solutions.

## EXPERIMENTAL AND COMPUTATIONAL METHODS

Samples of benzophenone (BP), ketoprofen (KP), and 1,4-dibenzoylbenzene (14DBB) were obtained from Aldrich (>99% purity), and the 3-(hydroxymethyl) benzophenone (3-HMBP) compound was synthesized following the methods detailed previously in the literature.<sup>39</sup> Perchloric acid was acquired from ACS reagent ( $\text{HClO}_4$  approx 70%). Spectroscopic-grade acetonitrile (MeCN), isopropanol, and deionized water were used as solvents to prepare sample solutions for the experiments presented in this work.

**Femtosecond Transient Absorption (fs-TA) Experiments.** The fs-TA experiments were done employing an

experimental setup and methods detailed previously,<sup>36</sup> and only a brief description is provided here. Fs-TA measurements were done using a femtosecond regenerative amplified Ti:sapphire laser system in which the amplifier was seeded with the 120 fs laser pulses from an oscillator laser system. The laser probe pulse was produced by utilizing ~5% of the amplified 800 nm laser pulses to generate a white-light continuum (350–800 nm) in a  $\text{CaF}_2$  crystal, and then this probe beam was split into two parts before traversing the sample. One probe laser beam goes through the sample while the other probe laser beam goes to the reference spectrometer in order to monitor the fluctuations in the probe beam intensity. For the experiments discussed in this work, a 40 mL solution was flowed through a 2 mm path-length cuvette. This flowing sample was then excited by a 267 nm pump laser beam. An absorbance of sample at 267 nm was used for the sample solutions for the fs-TA experiments in order to maintain the same number of photons being absorbed for the same irradiating conditions for the samples.

**Nanosecond Transient Absorption (ns-TA) Experiment.** Nanosecond time-resolved transient absorption (ns-TA) measurements were carried out with a LP920 laser flash spectrometer provided by Edinburgh Instruments Ltd. The probe light source is a 450 W ozone-free Xe arc lamp with 10 Hz to single shot operation versatile sample chamber with integral controller, high speed pump, and probe port shutters, sample holder, and filter holders, which produces a continuous spectrum between 150 to 2600 nm. Measurements of the ns-TA spectra were performed according to the following procedure. The fresh sample solutions were excited by a Q-switched Nd:YAG laser (4th harmonic line at  $\lambda = 266$  nm). The probe light from a pulsed xenon arc lamp was passed through various optical elements, samples, and a monochromator before being detected by a fast photomultiplier tube and recorded with a TDS 3012C digital signal analyzer. In the kinetics mode, a photomultiplier detector or InGaAs PIN detector is used and the transient signal acquired using a fast, high-resolution oscilloscope. In the spectral mode, an array detector is fitted to the spectrograph exit port to measure a full range of wavelengths simultaneously. Unless specified otherwise, the ns-TA experiments were performed in air-saturated solutions, and the sample solutions were made up to have an absorbance of 1 at 266 nm.

**Nanosecond Time-Resolved Resonance Raman (ns-TR<sup>3</sup>) Experiments.** ns-TR<sup>3</sup> experiments were done employing an experimental setup and methods detailed previously<sup>37</sup> and only a brief description is provided here. The fourth harmonic of a Nd:YAG nanosecond pulsed laser supplied the 266 nm pump wavelength and the 319.9 nm probe wavelength came from the third anti-Stokes hydrogen Raman-shifted laser line produced from the second harmonic of a second Nd:YAG laser for BP, KP, and 3-HMBP, and a 368.9 nm probe wavelength came from the second Anti-Stokes hydrogen Raman-shifted laser line produced from the second harmonic of a second Nd:YAG laser for the 14DBB experiments. The pump pulse photoexcited the sample to start the photochemical processes, and the probe pulse monitored the sample and the intermediate species formed. The laser beams were lightly focused and lined up so that they merged together onto a flowing sample. A pulse delay generator was utilized to electronically set the time delay between the pump and probe laser pulses. The Raman scattered signal was collected using a backscattering geometry and observed by a liquid nitrogen-cooled charge-coupled device (CCD) detector. The ns-TR<sup>3</sup> spectra shown here were found

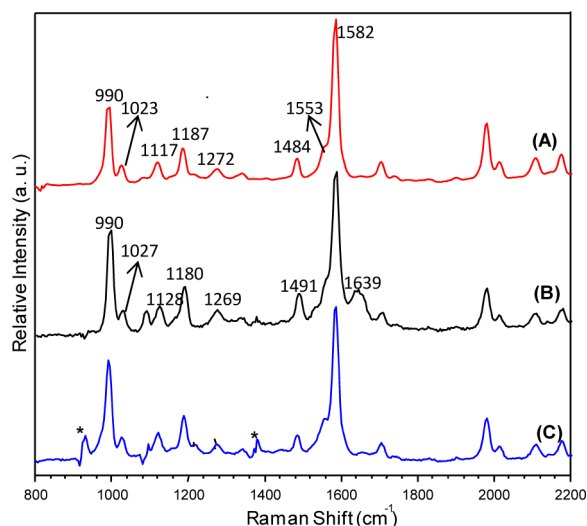
from subtraction of an appropriately scaled probe-before-pump spectrum from the correlated pump–probe resonance Raman spectrum to mostly get rid of the nontransient bands. The Raman bands of MeCN were used to calibrate the Raman shifts with an estimated uncertainty of  $5\text{ cm}^{-1}$ . The sample concentrations in ns-TR<sup>3</sup> were  $\sim 5 \times 10^{-4}\text{ M}$ .

**Density Functional Theory (DFT) Calculations.** DFT calculations were performed employing the (U)B3LYP method with a 6-311G(d,p) basis set. The Raman spectra were found from computing the Raman intensities from transition polarizabilities computed by numerical differentiation, with an assumed zero excitation frequency. A Lorentzian function with a  $15\text{ cm}^{-1}$  bandwidth for the vibrational frequencies and a frequency scaling factor of 0.974 was used in the comparison of the calculated results with the experimental spectra.<sup>40</sup> No imaginary frequency modes were observed at the stationary states of the optimized structures. All of the calculations were done using Gaussian 09.<sup>41</sup>

## RESULTS AND DISCUSSION

**Generation of the DPK Radical from <sup>3</sup>BP in Neutral Aqueous Solution.** Although many studies have been conducted on the photochemistry and photophysics of BP in different organic solvents, there are relatively fewer investigations using time-resolved vibrational spectroscopy to study the photochemical reactions of BP.<sup>27,31</sup> Here, nanosecond time-resolved resonance Raman spectroscopy (ns-TR<sup>3</sup>) has been used to obtain vibrational spectroscopic information for the structure and dynamics of the intermediates of BP in different solvents. Figure 1 shows the experimental ns-TR<sup>3</sup> spectra of BP in isopropanol, neutral aqueous, and acidic solutions acquired at a delay time at 120 ns. Previous investigations found that the singlet excited state of BP would efficiently undergo ISC to give rise to the <sup>3</sup>BP species with a  $n,\pi^*$  character. The active center of <sup>3</sup>BP localizes at the carbonyl group so that the  $n,\pi^*$  <sup>3</sup>BP

species has a high ability to abstract a hydrogen atom from strong hydrogen donors (such as alcohols and amines) to produce a DPK radical.<sup>30,42–44</sup> ns-TR<sup>3</sup> experiments for BP carried out in isopropanol solvent demonstrated that the <sup>3</sup>BP was quickly quenched by isopropanol, and the DPK radical was detected at a very early nanosecond delay time.<sup>31</sup> Figure 1A presents the ns-TR<sup>3</sup> spectrum of the DPK radical obtained in isopropanol. The main Raman bands of the DPK radical appear at 990, 1023, 1117, 1187, 1272, 1484, 1553, and  $1582\text{ cm}^{-1}$ . The  $990\text{ cm}^{-1}$  Raman band is associated with ring-breathing motions. The 1023, 1117, 1187, 1272, and  $1484\text{ cm}^{-1}$  Raman bands mainly have contributions from C–H bending motions. The 1553 and  $1582\text{ cm}^{-1}$  Raman bands have contributions mainly from C=C stretching motions. Interestingly, ns-TR<sup>3</sup> experiments of BP also demonstrated that the DPK radical was generated in neutral aqueous solution even though the water is a weak hydrogen donor. Figure 1C shows the ns-TR<sup>3</sup> spectrum of BP obtained at 120 ns in neutral aqueous solution. The experimental ns-TR<sup>3</sup> spectrum of BP in neutral aqueous solution is strikingly similar to that of BP obtained in isopropanol. This demonstrates that the DPK radical was also generated in neutral aqueous solution. Ledger and Porter<sup>16</sup> also reported that the DPK radical can be observed in aqueous solutions, but the mechanism for the formation of the DPK radical remains unclear. Knoll and co-workers<sup>45</sup> carried out the flash photolysis experiments aiming at understanding the formation mechanism of the ketyl radical from <sup>3</sup>BP in pure water and basic solutions. They concluded that the DPK radicals were formed in combined charge and proton transfer steps. Bensasson and co-worker<sup>22</sup> used the technique of time-resolved laser flash spectroscopy to study the photophysical and photochemical properties of <sup>3</sup>BP in water and acetonitrile. They determined the quantum yield of the ketyl radical formation in pure water and found some evidence for a hydrogen abstraction from water by <sup>3</sup>BP. Some of our previous studies also observed formation of ketyl radicals after photoexcitation of BP and some BP derivatives in water and some aqueous solutions.<sup>31–33</sup> If the formation of the ketyl radicals occurred by a hydrogen abstraction, it can be argued that this is an unprecedented and presumably highly endergonic process. Free-energy changes for abstracting a hydrogen atom and the generation of an OH radical from water by <sup>3</sup>BP may be calculated roughly using the Rehm–Weller equation.<sup>46</sup>



**Figure 1.** A comparison is shown of the experimental ns-TR<sup>3</sup> spectrum of BP in an isopropanol solvent acquired at a delay time of (A) 120 ns, the experimental ns-TR<sup>3</sup> spectrum of BP in acidic MeCN:H<sub>2</sub>O 1:1 (containing 0.5 M HClO<sub>4</sub>) mix solution acquired at a delay time of (B) 120 ns and the experimental ns-TR<sup>3</sup> spectrum of BP in neutral MeCN:H<sub>2</sub>O 1:1 mix solution acquired at a delay time of (C) 120 ns. The asterisks (\*) mark regions affected by solvent subtraction artifacts and/or stray light.

$$\Delta G = 96.5[E^{\circ}(D^{\bullet+}/D) - E^{\circ}(A/A^{\bullet-})] - \Delta E^{\infty} \quad (\text{kJ} \times \text{mol}^{-1})$$

Where  $E^{\circ}(D^{\bullet+}/D)$  is the one-electron reduction potential of the OH radical (ca. 2.75 V vs SCE<sup>47</sup>);  $E^{\circ}(A/A^{\bullet-})$  and  $\Delta E^{\infty}$  are the one-electron reduction potential and the triplet state energy of BP, respectively. As determined previously, the electron transfer for BP is  $292.6\text{ kJ mol}^{-1}$ ,<sup>48</sup> and the one-electron reduction potential of <sup>3</sup>BP is about  $E^{\circ}(A/A^{\bullet-}) = -1.245\text{ V}$  versus SCE.<sup>48</sup> With the use of data from Schwarz's<sup>49</sup> study, it can be estimated that the free energy of the abstraction of a hydrogen atom and the generation of an OH radical from water photolysis by <sup>3</sup>BP is roughly  $G = 93\text{ kJ/mol}$ . These numbers provide only an estimate for the thermochemistry for the hydrogen abstraction of <sup>3</sup>BP from water molecules. Some claims for a hydrogen abstraction from water by the <sup>3</sup>BP species have been disputed, and it was shown that no free OH radicals were formed.<sup>50</sup> Until now, the mechanism for the DPK radical formation observed by several different groups over the past 40

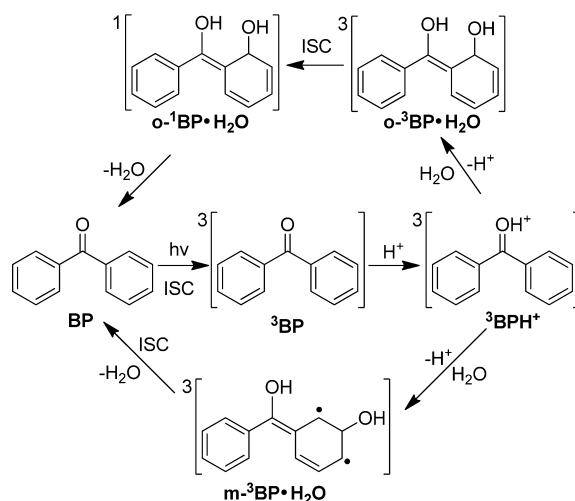


282 years remains unclear and there appears a lack of direct and  
 283 convincing evidence to uncover the mechanism for the  
 284 formation of DPK radicals in aqueous solution. This challenge  
 285 motivated us to conduct additional work on BP and its  
 286 derivatives, in particular, additional time-resolved resonance  
 287 Raman spectroscopy data, which are shown in succeeding  
 288 sections.

289 **Protonation-Induced Generation of the DPK Radical**  
 290 **for 1,4-Dibenzoylbenzene and the Photohydration**  
 291 **Reaction of  $^3\text{BP}$  in Acidic Aqueous Solutions.** BP is a  
 292 weak base in the ground state, and its protonation requires a  
 293 very strong acid. However, the acidity of the conjugate acid,  $\text{p}K_{\text{a}}$   
 294 ( $S_0$ ) =  $-4.7$  is reduced by 4 orders of magnitude in the excited  
 295 triplet state  $\text{p}K_{\text{a}}$  ( $T_1$ ) =  $-0.4$ .<sup>27</sup> Even so, the protonation of  $^3\text{BP}$   
 296 is still much slower than the usual oxygen-protonation reaction,  
 297 thus the protonation of the carbonyl is the rate-determining  
 298 step in preceding the fast hydration of the aromatic nucleus.<sup>27</sup>  
 299 The hydrated intermediates regenerate BP after ISC, the  
 300 protonation in inducing the hydration reaction is responsible  
 301 for the quenching of the aromatic ketones by protons from an  
 302 acidic aqueous solution, which will reduce the quantum yields  
 303 of their usual reactions. It does, however, switch on the  
 304 possibility to some novel photoreactions of substituted  
 305 aromatic ketones in acidic aqueous solution.<sup>51,52</sup> In order to  
 306 investigate the photohydration of BP and characterize the  
 307 properties of the intermediates of BP in acidic aqueous  
 308 solution, ns-TR<sup>3</sup> experiments have been carried out on BP and  
 309 we found that the  $^3\text{BP}$  can be observed at very early  
 310 nanosecond delay times.<sup>31</sup> Then the carbonyl of BP is  
 311 protonated, and the positive charge in the carbonyl group  
 312 transfers to the ortho- and meta-positions of the benzene ring,  
 313 hence the ortho- and meta-positions of benzene ring become  
 314 susceptible to be attacked by water molecules to generate the  
 315  $m\text{-}^3\text{BP}\cdot\text{H}_2\text{O}$  and  $o\text{-}^3\text{BP}\cdot\text{H}_2\text{O}$  hydrated intermediates.<sup>27</sup> As  
 316 shown in Figure 1B, the ns-TR<sup>3</sup> spectrum acquired at 120 ns  
 317 exhibits some noticeable differences compared with that of  
 318 DPK radical acquired in a neutral aqueous solution and an  
 319 isopropanol solvent. There are two new Raman bands growing  
 320 in at 1491 and 1639  $\text{cm}^{-1}$  that are the characteristic Raman  
 321 features of the  $m\text{-}^3\text{BP}\cdot\text{H}_2\text{O}$  and  $o\text{-}^3\text{BP}\cdot\text{H}_2\text{O}$  species, respectively.  
 322 The 1491 and 1639  $\text{cm}^{-1}$  Raman bands have major  
 323 contributions from the aromatic ring C–C stretching motions.  
 324 Therefore, this data demonstrates that  $^3\text{BP}$  will undergo the  
 325 photohydration reaction under acidic ( $\text{pH} = 0$ ) solution.<sup>31</sup> On  
 326 the basis of Zimmerman's ortho–meta effect for the benzene  
 327 ring site activation in photochemical reactions, these two sites  
 328 having a positive charge character can be attacked by water to  
 329 produce the short-lived hydration intermediates ( $o\text{-}^3\text{BP}\cdot\text{H}_2\text{O}$   
 330 and  $m\text{-}^3\text{BP}\cdot\text{H}_2\text{O}$ ) that subsequently deactivate to the ground  
 331 state ( $o\text{-}^1\text{BP}\cdot\text{H}_2\text{O}$ ) or proceed directly to the parent BP  
 332 molecule by dehydration reactions. Scheme 1 shows the  
 333 proposed photohydration reaction mechanism of BP in acidic  
 334 aqueous solution.

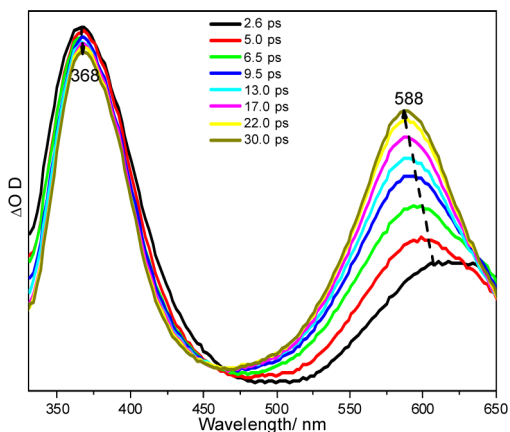
335 In fact, the characteristic Raman band at 1582  $\text{cm}^{-1}$  of the  
 336 DPK radical still can be observed in acidic aqueous solution.  
 337 This implies that the DPK radical is also detected in acidic  
 338 aqueous solution as well as the  $m\text{-}^3\text{BP}\cdot\text{H}_2\text{O}$  and  $o\text{-}^3\text{BP}\cdot\text{H}_2\text{O}$   
 339 hydrated intermediates. In order to find out whether the  
 340 protonation of  $^3\text{BP}$  can also promote the generation of the  
 341 DPK radical, we have selected a BP derivative with a large  
 342 substitution group at the para position in the benzene ring  
 343 because the electronic and steric effect may be able to block or  
 344 substantially hinder the photohydration reaction in acidic

**Scheme 1. Photohydration Reaction Pathways of BP in Acidic Aqueous Solution Proposed by Wirz and Coworkers.<sup>27</sup>**



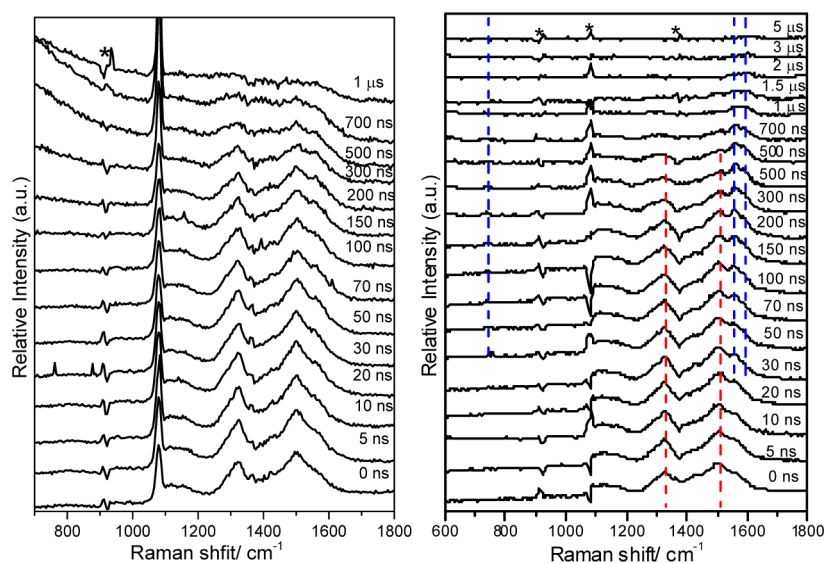
aqueous solution. 1,4-Dibenzoylbenzene (denoted as 14DBB) 345  
 was used as a model BP derivative where the para position is 346  
 substituted by a large benzoyl group. 347

Femtosecond transient absorption (fs-TA) experiments for 348  
 14DBB demonstrate that the first excited state undergoes ISC 349  
 to form the triplet state within 60 ps (see Figure 2). At a later 350

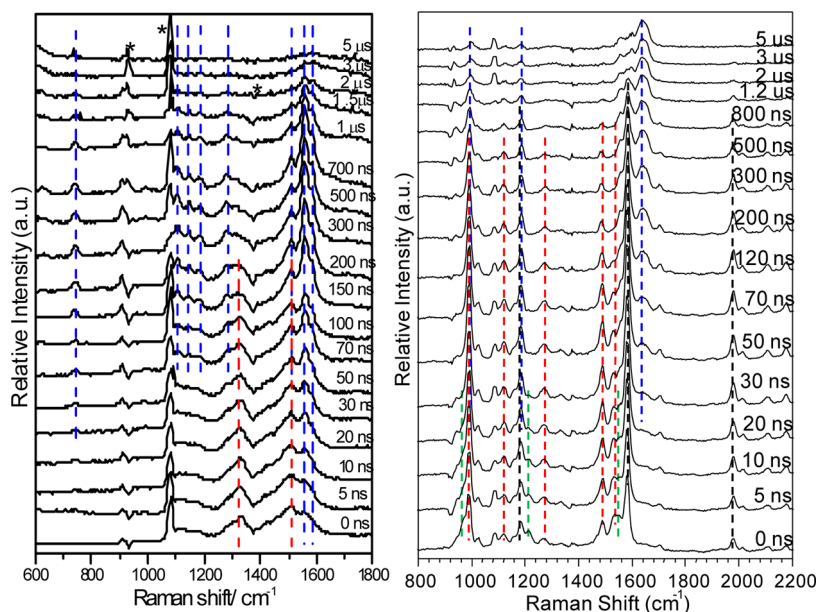


**Figure 2. Transient absorption spectra of 14DBB at early picosecond times recorded with 267 nm excitation in an acetonitrile solvent.**

delay time, one species with its main absorption bands at 368 351  
 and 590 nm remains until 3 ns. Figure 3 (left) displays ns-TR<sup>3</sup> 352  
 of 14DBB obtained in acetonitrile. Inspection of Figure 3 found 353  
 that only one intermediate was observed from 0 ns to 1  $\mu\text{s}$ . In 354  
 accordance with the preceding results of fs-TA experiment, the 355  
 intermediate detected by the ns-TR<sup>3</sup> spectra is likely the triplet 356  
 state of 14DBB ( $^3\text{14DBP}$ ). To confirm the assignment of 357  
 $^3\text{14DBB}$ , DFT calculations were done to predict its Raman 358  
 spectrum. The good agreement between the experimental ns- 359  
 TR<sup>3</sup> spectrum at 0 ns and the DFT calculation predicted 360  
 Raman spectrum of  $^3\text{14DBB}$  implies that the intermediate 361  
 observed in the acetonitrile solution can be assigned to the 362  
 $^3\text{14DBB}$  species (see Figure 1S of the Supporting Information). 363  
 Figure 3 (right) shows the ns-TR<sup>3</sup> spectra of 14DBB obtained 364  
 in a MeCN:H<sub>2</sub>O 1:1 solution. Examination of Figure 3 365  
 indicates that the first intermediate observed in neutral aqueous 366



**Figure 3.** Shown are the ns-TR<sup>3</sup> of 14DBB obtained in acetonitrile (left) and in MeCN:H<sub>2</sub>O 1:1 solution (right) using 266 nm as the pump laser wavelength and 368.9 nm as the probe laser wavelength. The asterisk (\*) mark subtraction artifacts.

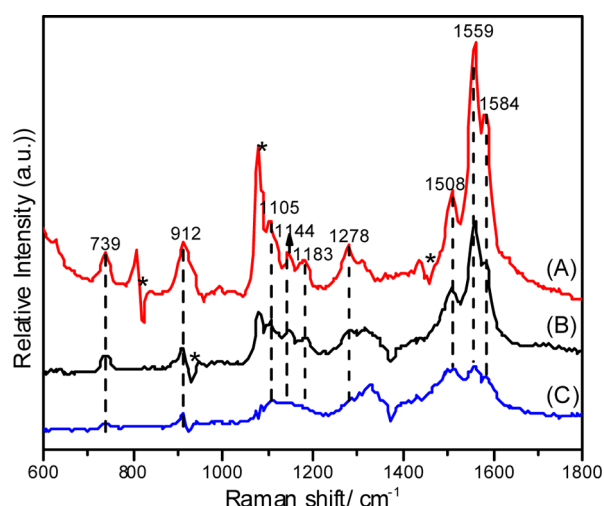


**Figure 4.** ns-TR<sup>3</sup> spectra of 14DBB in acidic MeCN:H<sub>2</sub>O (1:1 by volume, pH = 0) obtained with a 266 nm pump excitation wavelength and a 368.9 nm probe wavelength (left) and ns-TR<sup>3</sup> spectra of BP in acidic MeCN:H<sub>2</sub>O (1:1 by volume, pH = 0) obtained with a 266 nm pump excitation wavelength and a 319.9 nm probe wavelength (right) at various delay times that are indicated next to the spectra. The asterisk (\*) mark subtraction artifacts.

solution is the <sup>3</sup>14DBB species. As the decay of <sup>3</sup>14DBP (indicated by the red dotted line), a new intermediate can be detected at a later delay time (indicated by the blue dotted line). In order to make the assignment of the new species in aqueous solution, the ns-TR<sup>3</sup> experiment was also performed in an isopropanol solvent and this data is shown in Figure 2S of the Supporting Information. It is well-known that the <sup>3</sup>BP can abstract a hydrogen atom from isopropanol to produce the DPK radical, so we suspect that the <sup>3</sup>14DBB would also abstract a hydrogen atom from isopropanol to form a similar DPK radical. Figure 3S of the Supporting Information shows the comparison between the experimental ns-TR<sup>3</sup> spectrum of 14DBB obtained in isopropanol and the DFT calculation predicted Raman spectrum of the 14DBB ketyl radical. The

experimental spectrum exhibits significant similarity for the vibrational frequency pattern with the DFT predicted Raman spectrum of the 14DBB ketyl radical. Therefore, the intermediate detected in isopropanol is assigned to the 14DBB ketyl radical. Examination of the ns-TR<sup>3</sup> spectra obtained in a neutral aqueous solution and in an isopropanol solution indicates that the second new species obtained in the neutral aqueous solution can also be assigned to the 14DBB ketyl radical. Since the 14DBB ketyl radical can be observed in a neutral aqueous solution, we further carried out a ns-TR<sup>3</sup> experiment of 14DBB in acidic aqueous solution. Figure 4 presents ns-TR<sup>3</sup> spectra of 14DBB (left) and BP (right) obtained in pH = 0 acidic aqueous solution. Inspection of the ns-TR<sup>3</sup> spectra of BP in acidic aqueous solution in the previous

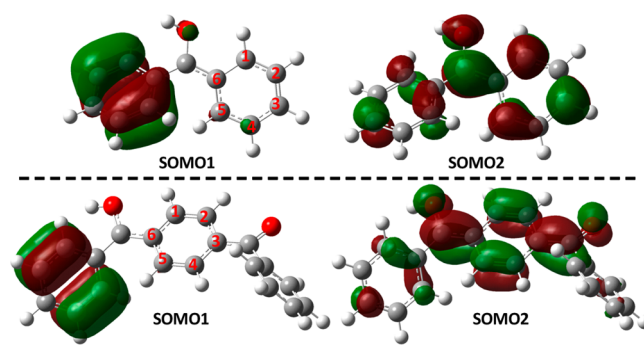
section found that the hydrated intermediates  $m$ - $^3\text{BP}\cdot\text{H}_2\text{O}$  and  $o$ - $^3\text{BP}\cdot\text{H}_2\text{O}$  are conspicuously present (indicated by the red dashed line and the blue dashed lines, respectively), except for the observation of the  $^3\text{BP}$  species at early delay times (indicated by the green dashed line) and the DPK radical at later delay times (indicated by the black dashed line). However, only two intermediates can be detected here, even in the acidic aqueous solution for 14DBB. The first intermediate is  $^3\text{14DBB}$  (indicated by red dashed line), and the second intermediate is the 14DBB ketyl radical (indicated by the blue dashed line). As hypothesized, the Raman signals of the hydrated intermediates cannot be detected, which demonstrates that no noticeable hydration reaction occurred for the  $^3\text{14DBB}$  species in the acidic aqueous solution. In addition, the Raman signal of the 14DBB ketyl radical acquired in the acidic aqueous solution is obviously enhanced in comparison with the signal of the 14DBB ketyl radical obtained in the neutral aqueous solution (see Figure 5). The  $739\text{ cm}^{-1}$  Raman band is assigned to a



**Figure 5.** (A) A comparison is shown of the experimental ns-TR<sup>3</sup> spectrum of 14DBB in an isopropanol solvent acquired at a delay time of 200 ns, (B) the experimental ns-TR<sup>3</sup> spectrum of 14DBB in acidic MeCN:H<sub>2</sub>O 1:1 (pH = 0) mix solution acquired at a delay time of 200 ns, and (C) the experimental ns-TR<sup>3</sup> spectrum of 14DBB in neutral MeCN:H<sub>2</sub>O 1:1 solution acquired at a delay time of 200 ns. The asterisk (\*) marks regions affected by solvent subtraction artifacts and/or stray light.

mode associated mostly with ring deformation motions. The  $912\text{ cm}^{-1}$  Raman band is associated with a mode that has mainly contributions from ring breathing motions. The  $1105$ ,  $1144$ , and  $1183\text{ cm}^{-1}$  Raman bands mainly have contributions from C–H bending in plane motions. The  $1278\text{ cm}^{-1}$  Raman band is assigned to a mode with major contributions from C–C stretching motions. The  $1508$ ,  $1559$ , and  $1584\text{ cm}^{-1}$  Raman bands are assigned to modes with mostly contributions from aromatic C=C stretch motions. As for BP, the  $^3\text{BP}$  was definitely protonated in the pH = 0 aqueous solution, and the protonated  $^3\text{BPH}^+$  was easy to be attacked at the ortho- and meta-positions of the benzene ring based on the Zimmerman's ortho–meta effect for the benzene ring site activation in the photochemical reaction, which would produce the  $o$ - $^3\text{BP}\cdot\text{H}_2\text{O}$  and  $m$ - $^3\text{BP}\cdot\text{H}_2\text{O}$  hydrated intermediates.<sup>27,31</sup> But for  $^3\text{14DBB}$ , the protonation does not trigger the photohydration reaction in noticeable amounts at the ortho- and meta-positions. This demonstrates that the benzoyl group at the *para* position of the

benzene ring successfully hinders the photohydration reaction to take place at the *meta*- and *ortho*-positions, although the protonated ketone has some of the Zimmerman's ortho–meta effect for the benzene ring site activation. Whereas, the enhanced resonance Raman signal of the 14DBB ketyl radical in the pH = 0 acidic aqueous solution suggests that the protonation of  $^3\text{14DBB}$  ( $^3\text{14DBBH}^+$ ) undergoes a photo-reduction reaction to transform into the 14DBB ketyl radical. To better understand the photohydration and photoreduction reactions that take place for  $^3\text{BPH}^+$  and  $^3\text{14DBBH}^+$  intermediates, we also examined the singly occupied molecular orbital (SOMO) of these key intermediates. The frontier orbitals for  $^3\text{BPH}^+$  and  $^3\text{14DBBH}^+$  obtained from the DFT calculations are shown in Figure 6. The frontier molecular



**Figure 6.** SOMO1 and SOMO2 frontier orbitals for  $^3\text{BPH}^+$  (top) and  $^3\text{14DBBH}^+$  (bottom) obtained from the DFT calculations.

orbitals comprising the SOMO1 to the SOMO2 contribute to their excited-state transitions. Inspection of Figure 6 reveals that the SOMO1 orbitals of  $^3\text{BPH}^+$  and  $^3\text{14DBBH}^+$  are almost the same with a  $\pi$ -type symmetry. However, the SOMO2 orbital of  $^3\text{BPH}^+$  (top) and  $^3\text{14DBBH}^+$  exhibits noticeably different electron density. For  $^3\text{BPH}^+$ , the electron density mainly resides on the C1 (ortho) and C3 (para) atoms, and the electron density on the C2 (meta) atom is less. The positive charge character of the meta position leads the meta position to be accessibly attacked by the water molecule, which facilitates the photohydration reaction for the  $^3\text{BPH}^+$  intermediate. While for the SOMO2 orbital of  $^3\text{14DBBH}^+$ , the electron density mainly locates on the phenyl ring containing the benzoyl substituent. Therefore, the meta position electron density is not favorable to proceed for the photohydration reaction for the  $^3\text{14DBBH}^+$  intermediate and prefers to undergo the photo-reduction reaction to produce the ketyl radical species unlike the  $^3\text{BPH}^+$  species that undergoes the photohydration reaction. The benzoyl moiety interaction with the benzophenone group in  $^3\text{14DBBH}^+$  appears to significantly change the electronic character and chemical reactivity of the ortho and meta sites of the benzophenone group compared to the parent  $^3\text{BPH}^+$  species. Knoll and co-workers concluded that the DPK radicals were formed via a combined charge and proton transfer step in a basic aqueous solution.<sup>45</sup> The ns-TR<sup>3</sup> of BP performed in a pH = 13 basic aqueous solution found that the radical anion of BP generated by the charge transfer was not observed, which have absorption bands at 335 and 600 nm.<sup>16</sup> Only the DPK radical was detected, and furthermore, the ns-TR<sup>3</sup> signal of the DPK radical was not enhanced. This implies that the charge transfer is not the initial step to induce the formation of the DPK radical. On the other hand, the generation of the DPK radical in neutral aqueous solution is not due to the reaction of  $^3\text{BP}$  with



s2.

the protonation of BP is the photoredox reaction first reported 507  
by Wan and co-workers.<sup>8,38,39,53–56</sup> This new type of 508  
photochemical reaction appears to occur for meta-substituted 509  
BP in an aqueous solution. The formal water-assisted 510  
photoredox reaction reduced the ketone to its corresponding 511  
alcohol, and then the meta-substituted alcohol moiety is 512  
oxidized to its aldehyde (or ketone), while these reactions were 513  
not detected for para-substituted BP derivatives. Here, the 3- 514  
(hydroxymethyl)benzophenone (denoted as 3-HMBP) mole- 515  
cule was investigated as a primary example for the protonation- 516  
induced formal water-assisted photoredox reaction in acidic 517  
solution. Photolysis of 3-HMBP in acidic (pH = 2) aqueous 518  
solution predominantly produced the major product 3- 519  
formylbenzhydrol (**2**) (95%) and small amounts of 3- 520  
formylbenzophenone (**3**) (5%) (see Scheme 3) with a quantum 521 523  
yield of about 0.6.<sup>54</sup> In an attempt to elucidate the photoredox 522  
mechanism of 3-HMBP, ns-TR<sup>3</sup> was utilized to investigate the 523  
possible intermediates formed after the photoexcitation of 3- 524  
HMBP in different solvents. In nonaqueous solvents (acetoni- 525  
trile and isopropanol) and neutral aqueous solution, 3-HMBP 526  
exhibits similar photochemistry to that of BP. Figure 7 shows 527 529

14DBB

$h\nu$

MeCN:H<sub>2</sub>O

$1^*14\text{DBB}$

ISC

$314\text{DBB}$

H<sup>+</sup>

electron transfer

14DBB ketyl radical

$314\text{DBBH}^+$

Figure 1 displays the Raman spectra of three samples: (A) pure PVP, (B) pure PAA, and (C) PVP/PAA hydrogel. The x-axis represents the Raman Shift in  $\text{cm}^{-1}$ , ranging from 800 to 1800. The y-axis represents the Relative Intensity in arbitrary units (a.u.).

Key Raman peaks are identified for each sample:

- (A) Pure PVP (Red line):** Shows characteristic peaks at 989  $\text{cm}^{-1}$ , 1176  $\text{cm}^{-1}$ , and 1584  $\text{cm}^{-1}$ . An asterisk (\*) marks a peak at approximately 1060  $\text{cm}^{-1}$ .
- (B) Pure PAA (Black line):** Shows characteristic peaks at 962  $\text{cm}^{-1}$  and 1518  $\text{cm}^{-1}$ .
- (C) PVP/PAA Hydrogel (Blue line):** Shows a prominent peak at 1584  $\text{cm}^{-1}$ , consistent with the PVP component.

**Figure 7.** (A) Comparison is shown for the experimental ns-TR<sup>3</sup> spectrum of 3-HMBP in isopropanol solvent acquired at a delay time of 120 ns, (B) the experimental ns-TR<sup>3</sup> spectrum of 3-HMBP in acidic MeCN:H<sub>2</sub>O 1:1 (pH = 2) mixed solution acquired at a delay time of 120 ns, and (C) the experimental ns-TR<sup>3</sup> spectrum of 3-HMBP in neutral MeCN:H<sub>2</sub>O 1:1 mixed solution acquired at a delay time of 120 ns. The asterisk (\*) marks regions affected by solvent subtraction artifacts and/or stray light.

**Protonation Induced Photoredox Reaction for 3-(Hydroxymethyl)benzophenone in Acidic Solution.** The protonation of <sup>3</sup>BP may induce the formation of the DPK radical and promote the photohydration at the ortho- and meta-positions in acidic aqueous solutions. The role of the protonation on other BP derivatives is also of concern as a precursor to other kinds of reactions that occur in acidic aqueous environments. One of the new reactions induced by

The reaction scheme illustrates the photochemical reaction of 1-phenyl-2-(hydroxymethyl)ethan-1-one (1) to 1-phenyl-2-(hydroxymethyl)ethan-1-one (2). The reaction proceeds via the formation of triplet intermediates 6 and 4, followed by proton transfer to form 5, and finally addition of water to form 7 and 2.

1-phenyl-2-(hydroxymethyl)ethan-1-one (1)  $\xrightarrow[h^+]{ISC}$  3-phenyl-2-(hydroxymethyl)ethan-1-one (6)  $\leftrightarrow$  3-phenyl-2-(hydroxymethyl)ethan-1-one (4)  $\xrightarrow[-H^+]{H_2O}$  3-phenyl-2-(hydroxymethyl)ethan-1-one (5)  $\xrightarrow{ISC}$  3-phenyl-2-(hydroxymethyl)ethan-1-one (7)  $\xrightarrow{H_2O}$  1-phenyl-2-(hydroxymethyl)ethan-1-one (2)

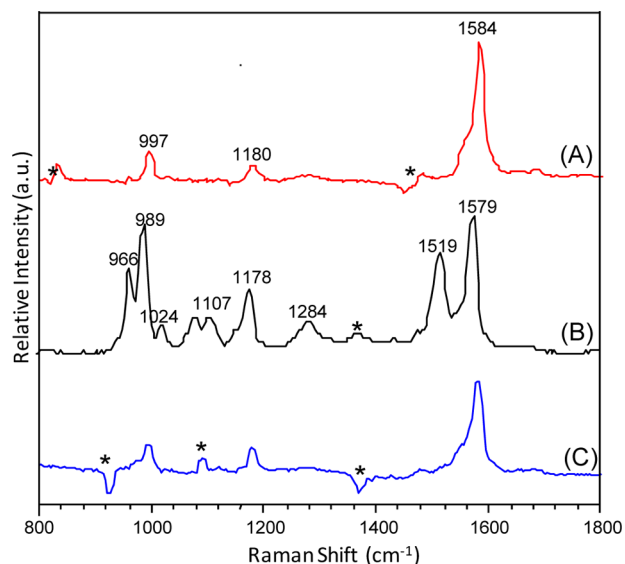
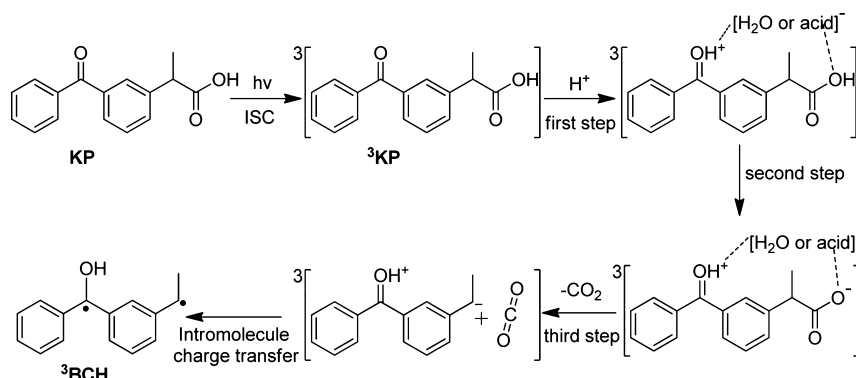


the comparison of experimental TR<sup>3</sup> spectra of 3-HMBP obtained in isopropanol and neutral aqueous solution at 120 ns. The excellent agreement between these two spectra demonstrates that the triplet state of 3-HMBP [<sup>3</sup>(3-HMBP)] generates the 3-HMBP ketyl radical by the combined steps of protonation and electron transfer in neutral aqueous solution, while it generates a 3-HMBP ketyl radical by a hydrogen abstraction reaction in isopropanol. However, in pH = 2 acidic solution, the protonation of <sup>3</sup>(3-HMBP) induces the photoredox reaction due to the meta-effect photochemistry. Further increasing the acidity to pH = 0, the protonation of <sup>3</sup>(3-HMBP) alternatively undergoes the photohydration reaction to produce the hydrated products, which are the same as the results for BP under the same conditions mentioned in the discussion above. Examination of Figure 7 found that two new peaks appear at 962 and 1518 cm<sup>-1</sup> in the pH = 2 acidic solution that are the characteristic Raman bands of the intermediate 5 from Scheme 3. The 962 cm<sup>-1</sup> Raman band is associated with a mode that mainly has contributions from ring breathing motions. The 1518 cm<sup>-1</sup> Raman band is assigned to a mode that has mostly contributions from aromatic C=C stretching motions. On the basis of the preceding results, the strong Raman band at 1584 cm<sup>-1</sup> may have contributions from transient species associated with both the photoredox reaction and the photoreduction reaction, while the Raman bands at 962 and 1518 cm<sup>-1</sup> probably have mainly contributions from intermediates involved in the photoredox reaction. The intensities of the new Raman bands at 962 and 1518 cm<sup>-1</sup> are much stronger in pH = 2 aqueous solution than that of the ones in pH = 4 and pH = 0 solutions. This implies that the efficiency of the photoredox reaction of <sup>3</sup>(3-HMBP) is higher in the pH = 2 aqueous solution than those in other conditions. Wirz and co-workers found that the efficiency of the photohydration reaction of BP in acidic aqueous solutions reached its maximum at the pH value of 0.<sup>27</sup> Since both of the photoredox reaction and photohydration reaction of 3-HMBP are initially induced by the protonation of ketone in acidic aqueous solution, it is necessary to determine which reaction is predominant under stronger acidic conditions. A later study reported that the photoredox reaction was not obvious in super strong acidic aqueous solutions with pH = 0 and below.<sup>56</sup> Examination of the ns-TR<sup>3</sup> spectra of 3-HMBP in pH = 0 solution suggests that the photoredox reaction can still be observed in pH = 0 aqueous solution, but the efficiency of the photoredox reaction significantly decreased compared to that in the pH = 2 aqueous solution using the criterion of the Raman features at 962 and 1518 cm<sup>-1</sup> as marker bands for the photoredox reaction. The change of the relative intensities of these marker bands in different pH acidic aqueous solutions implies that the photoredox reaction, the formation of ketyl radical from protonation species, and the photohydration reaction remarkably compete with each other, thus presumably one of them may be predominant under certain desired conditions. It seems that judicious control and exploration of the intermediate and reaction outcomes as a function of pH values may pave a way to find new reaction outcomes and to select reaction conditions to produce mainly one desired reaction outcome of those available. If the photohydration reaction is more favorable than the photoredox reaction in a pH = 0 aqueous solution, the efficiency of the photoredox reaction would increase relative to the photohydration reaction in a pH = 2 aqueous solution. Ns-TR<sup>3</sup> studies on 3-HMBP are consistent with the previous observations of Wirz and co-

workers<sup>27</sup> for BP and Wan and co-workers<sup>54,56</sup> for 3-HMBP in acidic aqueous solutions. An unusual and efficient photoredox reaction after the protonation of 2-(1-hydroxyethyl) 9,10-anthraquinone was also found in acidic aqueous solution.<sup>57</sup> The observation of protonated species in neutral and acidic aqueous solutions by fs-TA spectra indicated that the carbonyl oxygen was protonated initially, which acted as a precursor of this photoredox reaction. Ns-TR<sup>3</sup> results and DFT calculations suggested that protonation of the carbonyl group was the rate-determining step of the photoredox reaction, which preferred to occur under moderate acidic conditions compared with a neutral aqueous condition. To summarize, the selectivity of the photochemical reactions by varying the degrees of the acidity of an aqueous solution is practical for BP and a number of derivatives. Moreover, it can most likely be employed for other ketone containing compounds, which may open a new door into the discovery of new photochemistry and outcomes for a range of ketone compounds and may enable some ability to exert a degree of control of the photochemistry by controlling the pH of an acid aqueous solution.

**Protonation Induced Photodecarboxylation Reaction for Ketoprofen in Acidic Aqueous Solution.** Another type of photoreaction induced by the protonated triplet state of a ketone is the photodecarboxylation reaction of ketoprofen (KP) in a high water concentration solution or an acidic solution. KP is a benzophenone-derived drug that is often applied as a nonsteroidal anti-inflammatory drug (NSAID) but can undergo photosensitization reactions giving rise to unwanted phototoxic effects.<sup>58,59</sup> The rate of the decarboxylation reaction of KP exhibits a large dependence on the polarity of the solvent.<sup>60</sup> In addition, the polar protic solvent was proposed to be the donor of a proton or hydrogen to facilitate intramolecular proton transfer as the initial step to induce the photodecarboxylation.<sup>61</sup> Some studies suggested that only the dissociated triplet state of KP anion (<sup>3</sup>KP<sup>-</sup>) underwent decarboxylation in basic solution while the neutral form of triplet state of KP (<sup>3</sup>KP) did not undergo decarboxylation.<sup>32,62,63</sup> On the other hand, although several studies have been conducted for acid-catalyzed decarboxylation in the past,<sup>64–66</sup> few studies involving an acid modulated excited state intramolecular proton transfer (ESIPT) to induce the decarboxylation reaction have been reported until recently. In our recent ns-TR<sup>3</sup> studies for KP, the decarboxylation reaction of <sup>3</sup>KP was observed not only in aqueous solutions with a high water concentration but also in acidic aqueous solutions after 266 nm excitation.<sup>35,37</sup> KP exhibits photochemistry similar to that of BP in acetonitrile, isopropanol, and neutral aqueous solution with low water concentration (water volume ≤ 50%). Nevertheless, further increasing the concentration of water may lead KP to undergo a significant decarboxylation process, especially in solutions with a very high concentration of water (water:acetonitrile ≥ 9:1, v:v);<sup>35</sup> DFT calculations found that a water molecule bridge allows a proton to leave the carboxylate group so as to enable a simultaneous transfer of a proton to the carbonyl group. This solvent-mediated ESIPT subsequently leads to a decarboxylation reaction and formation of a triplet protonated biradical species observed in the ns-TR<sup>3</sup> experiments.<sup>37</sup> Therefore, the protonation of the carbonyl group of KP is the initial step to promote an intramolecular proton migration from the carboxylate group to the carbonyl group, which then induces the C–C cleavage of the decarboxylation process that is then followed by a very fast water-assisted rearrangement to generate

**Scheme 4. Proposed Mechanism for the ESIPT-Induced Decarboxylation Reaction of  $^3\text{KP}$  with the Assistance of Water Molecules or Acid in Aqueous Solutions**

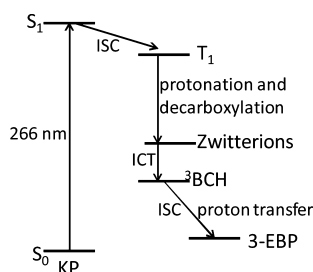


**Figure 8.** (A) Comparison of the experimental ns-TR<sup>3</sup> spectrum of KP in isopropanol solvent acquired at a delay time of 200 ns, (B) the experimental ns-TR<sup>3</sup> spectrum of KP in acidic MeCN:H<sub>2</sub>O 1:1 (pH = 0) mixed solution acquired at a delay time of 50 ns, and (C) the experimental ns-TR<sup>3</sup> spectrum of KP in neutral MeCN:H<sub>2</sub>O 1:1 mixed solution acquired at a delay time of 200 ns. The asterisk (\*) marks regions affected by solvent subtraction artifacts and/or stray light.

proton donor to the carbonyl group with energy barrier of 700  $-0.21$  kcal/mol. Thus, the benzophenone moiety is protonated 701 first to generate a cation. Second, the proton is transferred from 702 the carboxylate group to perchloric acid through a transition 703 state TS<sub>2</sub> with an energy barrier of 1.3 kcal/mol. Finally, a 704 zwitterionic form of KP is produced in which there is the 705 protonation of the carboxyl group and a dissociated carboxylate 706 group, and this species undergoes the C–C cleavage step that 707 subsequently releases CO<sub>2</sub>. Afterward, the intramolecular 708 charge transfer leads to a fast formation of the  $^3\text{BCH}$  709 intermediate. Therefore, in the acidic solution, the protonation 710 of the ketone induced the ESIPT that gives rise to the 711 subsequent decarboxylation process for  $^3\text{KP}$  in an acidic 712 solution. This mechanism is conspicuously different from the 713 decarboxylation mechanism of the triplet state of the KP anion 714 that takes place in a basic solution. To examine why the 715 protonated triplet state of KP ( $^3\text{KPH}^+$ ) does not undergo a 716 photohydration reaction as observed for BP but rather KP 717 experiences the photodecarboxylation reaction, DFT calcu-

lations were also done to estimate the energy barrier for the photohydration reaction. These results show that energy barriers of photohydration reaction at the ortho- and meta-positions are 12.3 and 6.4 kcal/mol, respectively. Given that the photohydration reaction has a higher energy barrier than the lower energy barrier (−0.21 kcal/mol) for the photodecarboxylation reaction, only the photodecarboxylation reaction may be expected to occur to a significant extent in an acidic solution, which is consistent with experimental observations for KP. An overall Jablonski-type diagram consistent with our results is displayed in Scheme 5 for the protonation and decarboxylation

**Scheme 5. Protonation and Decarboxylation Reaction Pathways of KP Excited by 266 nm in Acidic MeCN:H<sub>2</sub>O 1:1 (pH = 0) Mixed Solution**



reaction pathways of KP excited by 266 nm light in an acidic aqueous solution. KP was first excited to the S<sub>1</sub> state and then underwent a highly efficient ISC to convert into the T<sub>1</sub> state. After protonation of the carbonyl group of the triplet state in an acidic aqueous solution, the molecule will promptly experience a decarboxylation process to generate a zwitterionic form which accounts for the generation of the <sup>3</sup>BCH via intramolecular charge transfer (ICT) species. The <sup>3</sup>BCH species appears to undergo a water-assisted proton shift or an acid-assisted proton transfer and then radiationless decay to produce the singlet ground state 3-ethylbenzophenone (3-EBP) product.<sup>67,68</sup> The study of the ESIPT-induced decarboxylation of KP in acidic solution is interesting because it enables KP to be used as an efficient platform to release a leaving group for KP derivatives via a benzylic carbanion pathway but not via a biradical pathway.<sup>34</sup>

## CONCLUSION

The ns-TR<sup>3</sup> experimental results of this work indicate that protonation plays a crucial role for the photochemistry of BP and its derivatives in acidic solutions. In this study, a ns-TR<sup>3</sup> investigation of 14DBB in acidic solution provides direct evidence to support a mechanism that the protonation of the ketone and a subsequent electron transfer are the necessary steps to generate the ketyl radical for BP and its derivatives in acidic aqueous solutions. In addition, the protonation can be responsible for the quenching of an aromatic ketone in acidic aqueous solution. As for BP, except for the observation of the DPK radical, the protonation of the ketone makes the ortho- and meta-positions of the benzene ring become more susceptible to be attacked by water molecules to produce the hydrated intermediates *m*-<sup>3</sup>BP·H<sub>2</sub>O and *o*-<sup>3</sup>BP·H<sub>2</sub>O in a pH = 0 acidic aqueous solution. While for 3-HMBP, the protonation drives the triplet state to undergo a water-assisted photoredox reaction in a pH = 2 acidic aqueous solution. In contrast, the protonation leads <sup>3</sup>KP to go through a solvent-mediated ESIPT that transfers a proton from the carboxyl group to carbonyl

group in a neutral high water concentration solution or an acidic aqueous solution. Afterward, the zwitterionic form experiences the photodecarboxylation reaction to release a CO<sub>2</sub> and form a biradical species (<sup>3</sup>BCH). In conclusion, these novel photochemical reactions are initiated by protonation of the ketone, since the protonation will strongly destabilize the n,π\* state of the triplet state of BP and its derivatives. Thus, the protonation of the ketone in acidic aqueous solutions provides a powerful way to lead to the discovery of new photochemical outcomes depending on the properties of the substituents on the aromatic rings and control of the pH of the aqueous solution. It is worth noting that one may be able to turn on or off selective photoreactions via the protonation of substituted aromatic ketones by changing the pH value of the solvent.

## ASSOCIATED CONTENT

### Supporting Information

Optimized geometries and ns-TR<sup>3</sup> spectra of 14DBB obtained in an isopropanol solvent and the comparison of its experimental spectra with results from DFT calculation for the predicted spectra for the triplet state of 14DBB and the 14DBB ketyl radical. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This work was supported by grants from the Research Grants Council of Hong Kong (HKU 7048/11P) to D.L.P. Partial support from the Grants Committee Areas of Excellence Scheme (AoE/P-03/08) and the Special Equipment Grant (SEG HKU/07) are also gratefully acknowledged.

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