# Direct Observation of Triplet State Mediated Decarboxylation of the Neutral and Anion Forms of Ketoprofen in Water-Rich, Acidic, and PBS Solutions

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Ⓢ Supporting Information

ABSTRACT: The decarboxylation reaction of KP in different acetonitrile—water mixtures producing a carbanion or biradical intermediate is investigated by using femtosecond transient absorption and nanosecond time-resolved resonance Raman spectroscopies to unveil the mechanism of the photochemistry of KP. The irradiation of either the neutral or anion forms of KP leads to the excited singlet state KP species transforming into a corresponding triplet state KP species via a highly efficient intersystem crossing, and then, a triplet state mediated decarboxylation reaction occurs to generate a carbanion intermediate in the phosphate buffer solutions or a biradical species in the water-rich or acidic solutions examined here.
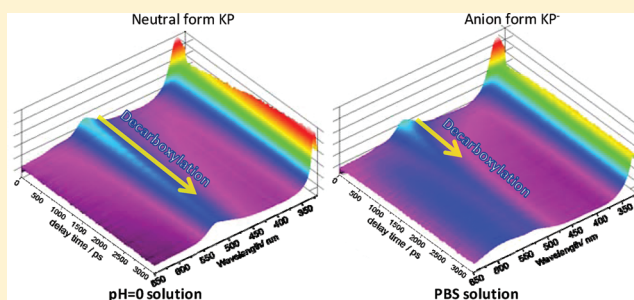
Ketoprofen (KP) is an important nonsteroidal anti-inflammatory drug (NSAID) used to treat musculoskeletal and joint disorders, osteoarthritis, rheumatoid arthritis, and other inflammatory conditions.[1] KP contains a benzophenone (BP) moiety and has a BP-like photochemistry under some environmental conditions.[2−4] KP has found utility as a NSAID for topical application but has limited usage due to the side effects resulting from phototoxic and photoallergic reactions such as photoinduced lipid peroxidation,[5] DNA damage,[6] and photohemolysis.[7] These unwanted side effects possibly result from the generation of short-lived intermediates like free radicals rather than from toxic photoproducts.[8] In order to better understand the phototoxic mechanism(s) of KP, much effort has been devoted to studying the photochemistry and phototoxicity of KP.[1,5,9−20] In addition to its use as a NSAID, KP has also found utility as a new platform for developing phototriggers and ketoprofenate photocages which were recently demonstrated to have a rapid and efficient photo-release with aqueous compatibility.[12] This KP type of photocage releases the leaving group via a new carbanion-mediated mechanism, and it is necessary to better understand how the carbanion is generated and whether it is a triplet or singlet mediated process.

The information on KP obtained so far by laser flash photolysis (LFP) is limited, and the results have been a matter of controversy.[13−18] KP usually undergoes two classes of photochemical reactions after irradiation: one pathway is to generate a ketyl radical in neutral aqueous solutions, while another pathway produces a carbanion intermediate by a decarboxylation reaction in basic solutions. For the generation of the carbanion intermediate, both singlet- and triplet-mediated decarboxylation reaction mechanisms have been proposed. Due to incomplete attempts to sensitize the formation of the triplet state KP (^{3}KP) in aqueous solutions by LFP, Scaiano and co-workers suggested that the carbanion precursor was either an excited singlet state or an extremely short-lived triplet.[19] Monti and co-workers suggested that the photochemistry of KP in aqueous solutions was a triplet-initiated decarboxylation that gave rise to a triplet biradical intermediate where the main process involved an intra-molecular electron transfer from the carboxyl (donor) to the carbonyl (acceptor) groups to induce an adiabatic decarbox-ylation.[14] For the neutral form KP, TD-DFT calculations of the excited state potential energy surfaces revealed that the neutral species would not decarboxylate easily, while the dissociated KP⁻ anion decarboxylates through the triplet state with a small 3−5 kcal/mol barrier from several low-lying excited singlet states.[20] Recent CASSCF/CASPT2 computations examined KP to map the pH- and wavelength-dependent pathways for the photodecarboxylation of KP.[21] This study found the decarbox-ylation of the anion form (KP⁻) was initiated by a long-distance charge transfer (CT) excited state when populated by photoexcitation at 330 nm. A short-distance CT excited state was predominant with photoexcitation at $\lambda < 260$ nm and appeared to be responsible for the decarboxylation of the neutral form KP.[21]
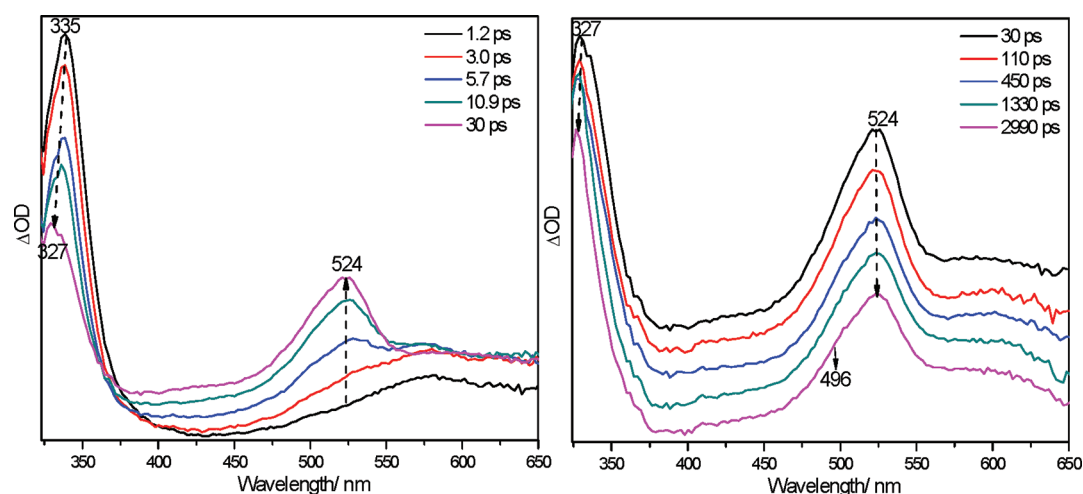
A recent study proposed a triplet excited state intramolecular proton transfer (ESIPT) induces the decarboxylation reaction of the neutral form KP in water-rich aqueous and strong acidic solutions.[22] However, the triplet state mediated decarboxylation
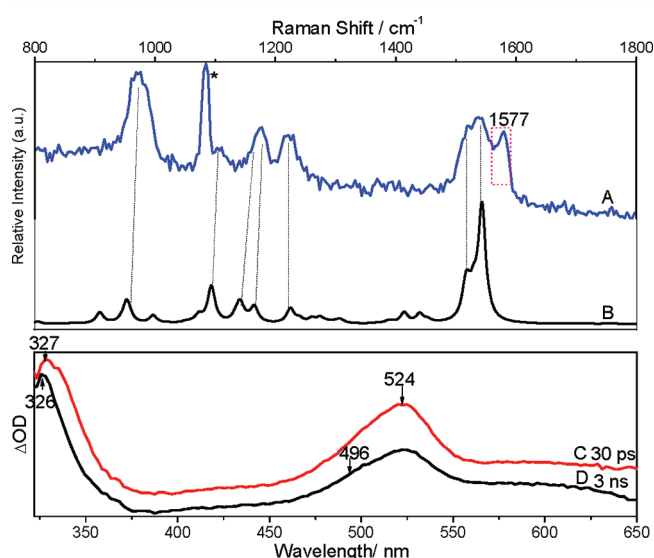
Figure 1. Transient absorption spectra of KP at early (left) and late (right) picosecond times recorded with 267 nm excitation in a MeCN:H$_2$O (2:8) solution.

reaction of KP was not unambiguously verified due to the lack of direct observation of the dynamics from the femtosecond to picosecond time scales for the decay of the ^{3}KP intermediate. In this study, we report a femtosecond transient absorption (fs-TA) study on the photochemistry of KP in different acetonitrile:water (MeCN:H$_2$O) mixtures, and these results indicate that the decarboxylation of KP in the water-rich, acidic, and phosphate buffer (PBS) solutions is a triplet-mediated process. These results in conjunction with the nanosecond time-resolved resonance Raman spectra (ns-TR^3) on KP provide convincing experimental evidence for the predominant triplet-mediated decarboxylation processes for both the neutral form KP and anion form KP$^-$ in aqueous solutions (although with significantly different reaction rates for the two different forms of KP) under acidic, neutral water-rich, and PBS conditions.

Previous investigations indicated that water was not necessary for the decarboxylation of KP.[15,23] In more recent work, results from the ns-TR^3 experiments found that a water-rich environment is a prerequisite to the efficient decarbox-ylation of the neutral form KP in aqueous solutions.[22] In order to elucidate the mechanism of the decarboxylation reaction of KP, fs-TA experiments were done in neat MeCN and MeCN:H$_2$O mixtures (volume ratio 9:1, 1:1, 2:8, respectively). At the beginning of 1 ps, a strong transient absorption at 335 nm accompanied by a broad shoulder peak at 570 nm is detected (see Figure 1). Subsequently, a new transient absorption gradually increases at 524 nm at the expense of transient absorption at 335 nm within 30 ps. In addition, the absorption at 335 nm exhibits a down-shift during the transformation. The transient absorptions at 335 and 570 nm are associated with the S$_1$ → S$_n$ transition absorption. The spectrum at 30 ps is characterized by a maximum sharp peak at 327 nm and a broad absorption peak extending from 450 to 600 nm with maxima at 524 nm which are similar in shape and intensity to that of KP observed by LFP studies in MeCN:H$_2$O mixtures, and these two transient absorption peaks are assigned to the lowest ^{3}KP species.[13−15] The spectral evolution of the intersystem crossing (ISC) from the singlet excited state to the triplet state has an about 10 ps time constant in 10% water solution, which is similar to that of BP obtained under MeCN solvent.[24] However, the time constant of ISC (about 5.9 ps) obtained in 80% water solution is faster than that of lower water

concentration solutions for KP (see the kinetics of early picosecond delay time in Figure 3); this reveals that the energy gap between S$_1$ and T$_1$ may be narrowed by the hydrogen bond effect in the high water concentration solutions. Figure 1 (right) presents the spectral evolution obtained in 80% water solution at later picosecond delay time. The different dynamics of the various characteristic wavelengths imply that a new species is expected to be generated, which is supported by the ns-TR^3 experiments that the ^{3}KP is only observed at the early nanosecond time and then a new species (triplet protonated carbanion biradical, ^{3}BCH) begins to be observed at early nanosecond delay times.[22,25] Figure 2 shows a comparison of the transient absorption of KP obtained at 30 ps and 3 ns along with a DFT calculation Raman spectrum of ^{3}KP and experimental resonance Raman spectrum obtained at 5 ns. The DFT calculation predicted Raman spectrum of ^{3}KP exhibits a good agreement with the experimental resonance Raman spectrum at 5 ns, and this combined with the fs-TA

Figure 2. Comparison of the ns-TR^3 spectrum obtained at 5 ns (A) and the DFT predicted Raman spectrum of ^{3}KP (B). Below is the transient absorption of ^{3}KP at 30 ps (C) and 3 ns (D) obtained in a MeCN:H$_2$O (2:8) solution.

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spectra demonstrates that the decay of the ^{3}KP species leads to production of a new species. The observation of the characteristic Raman band of 1577 cm^{-1} at 5 ns implies that the new species is the ^{3}BCH biradical intermediate generated by the decarboxylation reaction of ^{3}KP.[25] Since the ^{3}KP species can still be observed on the several nanosecond time-scale in the ns-TR^3 spectra, it appears that ^{3}KP has not yet completed its decay at 3000 ps. Therefore, the transient absorption at 3000 ps observed in the fs-TA spectra most likely has noticeable contributions from both the ^{3}KP and ^{3}BCH biradical species.

To investigate the decay dynamics of ^{3}KP being dependent on the water concentration, fs-TA experiments were conducted in the different ratios of MeCN:H$_2$O solutions. Figure 3 shows
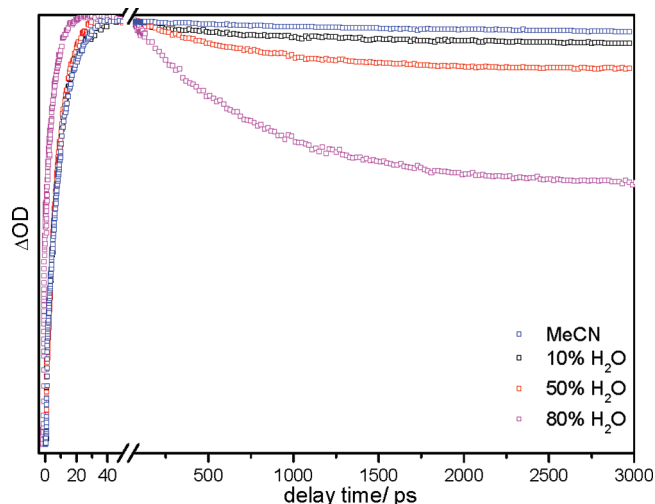

Figure 3. Shown are the normalized dynamics for the transient absorption of the ^{3}KP recorded at 524 nm in the different MeCN:H$_2$O mixtures.

the decay dynamics of ^{3}KP recorded at 524 nm in the different MeCN:H$_2$O mixtures. In pure MeCN solvent, the ^{3}KP intermediate is stable and does not decay discernibly within

3000 ps and the ^{3}KP may be observed by ns-TR^3 experiment within 250 ns.[26] In 10% water concentration solution, the ^{3}KP slightly decays in the picosecond time scale and has a ca. 119 ns lifetime; this coincides with the observation of ^{3}KP by ns-TR^3 experiments done in the same experimental conditions.[25,26] In 50% water solution, the decay time constant of the ^{3}KP intermediate is ca. 97 ns; the trend of the decay for the ^{3}KP in 50% water solution is faster than that of ^{3}KP in 10% water solution. This is mainly due to a process where the ^{3}KP predominantly produces a KP ketyl radical species via reaction with water molecules.[25] The same reaction of BP derivatives usually occurs on the nanosecond time scale.[14,15,25−30] Therefore, the decay curve of ^{3}KP is not significantly sharp even in a 50% water solution within 3000 ps. However, in a 80% water solution, the ^{3}KP dramatically decays to a large extent compared with the dynamics obtained in the lower water concentration solutions. This coincides with the lifetime of ^{3}KP obtained in 70% water solution being just ca. 46 ns which is obviously shorter than the one (ca. 97 ns) obtained in the 50% water solution.[25] The subsequent observation of the ^{3}BCH biradical at the resolution of the ns-TR^3 instrument implies that the ^{3}KP species should undergo the decarboxylation reaction on the subnanosecond time scale. Therefore, the triplet-mediated decarboxylation reaction of ^{3}KP is rationalized by the fast decay of ^{3}KP in the water-rich solutions.

We recently proposed that water and acid can assist the decarboxylation of ^{3}KP via a triplet excited state intramolecular proton transfer (ESIPT) in water-rich and acidic solutions.[22] The decarboxylation reaction is facile in the high water ratios (H$_2$O:MeCN ≥ 50%) or moderate and strong acidic solutions. The results obtained in the high water concentration solutions demonstrate that the ^{3}KP is the direct precursor for the decarboxylation of KP; that is, the triplet state mediated decarboxylation reaction of KP should possibly be a predominant pathway compared to the singlet-mediated decarboxylation pathway.[13] In an attempt to verify the neutral form ^{3}KP mediated decarboxylation reaction mechanism, the pump−probe experiments were also conducted in the acidic solutions. In a pH 1 solution (see Figure 7S, Supporting
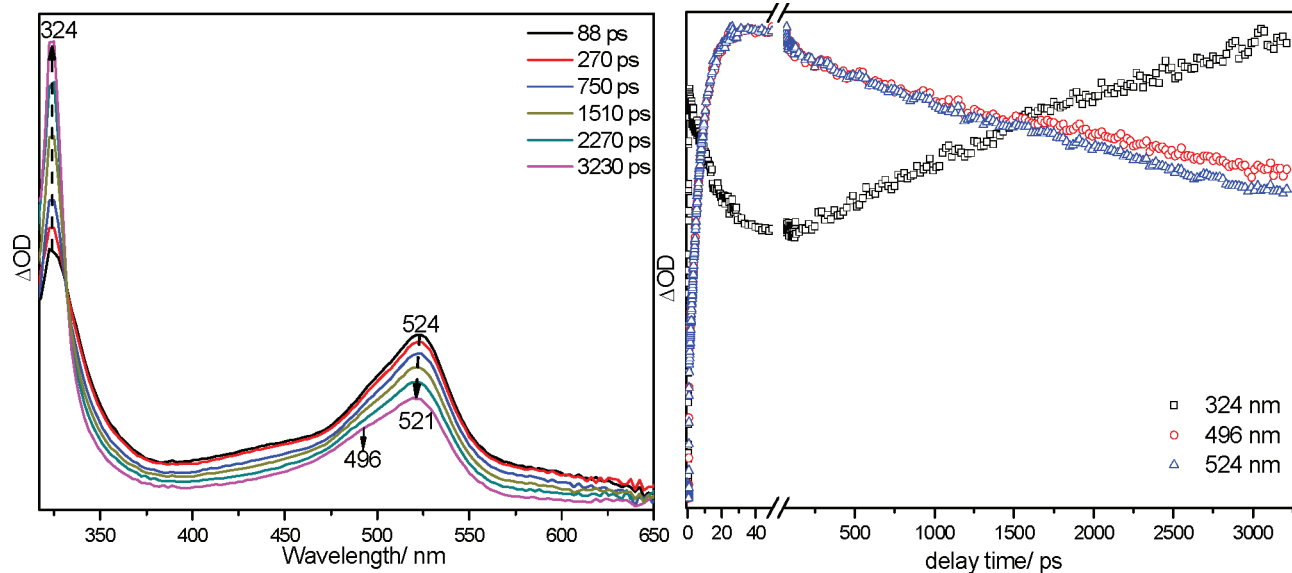
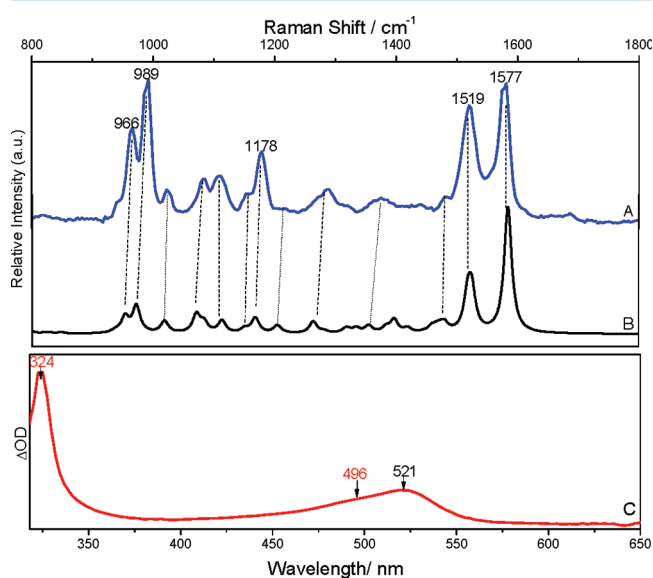**Figure 4.** Transient absorption spectra of KP at late picosecond times recorded with 267 nm excitation in an acidic MeCN:H$_2$O (1:1, pH 0) solution (left) and its corresponding normalized kinetics recorded at 324, 496, and 524 nm within 3200 ps (right).

Information), the ^{3}KP completely remains in the neutral form, while the ^{3}KP decreases with the increase of delay times. The decay of ^{3}KP and the observation of ^{3}BCH biradical within the resolution of ns-TR^3 experiments under analogous conditions[22] further verify the decarboxylation reaction initiated by the ^{3}KP with assistance of water or acid molecules. This is further supported by the DFT calculations that the perchloric acid could catalyze the decarboxylation reaction of ^{3}KP by an acid modulating the ESIPT process.[22] In a very strong acidic solution (pH 0) (see Figure 4), the singlet state initially transforms to the triplet state within 30 ps which is revealed by the decay kinetics of the 324 nm feature and the increasing growth kinetics of the 524 nm feature. Then, the ^{3}KP species decays so fast that the spectral evolution at 324 nm (which is attributed to the ^{3}BCH species) begins to increase with the simultaneous decay of the maximum absorption at 524 nm (which is attributed to ^{3}KP). The ^{3}KP species can still be observed by ns-TR^3 experiments in the MeCN:H$_2$O (1:1) pH 1 acidic solution. The growth time constant of the ^{3}BCH species under these conditions is 33 ns.[22] Therefore, the decay time constant of ^{3}KP in the pH 1 acidic solution should be close to 33 ns. However, the ^{3}KP is barely observed by the ns-TR^3 experiment done in the MeCN:H$_2$O (1:1) pH 0 acidic solution. Therefore, the fs-TA spectrum observed at 3200 ps in the pH 0 acidic solution has noticeable contributions mainly from the ^{3}BCH species accompanied by a smaller contribution from the ^{3}KP.

In addition, a weak shoulder transient absorption around 496 nm springs up at 3.2 ns. The assignment of the shoulder feature at 496 nm to the ^{3}BCH species is mainly based on the following observations. First, with the decay of the 524 nm band (which is the transient absorption of ^{3}KP), the shoulder band at 496 nm appears. This shoulder band is very close to the transient absorption seen at 504 nm obtained in a pH 0 perchloric acidic solution by nanosecond transient absorption (ns-TA) spectroscopy experiments.[22] On the nanosecond time scale, ns-TR^3 studies on KP in water-rich or acidic solutions convincingly make the assignment of the transient absorption at 504 nm to the ^{3}BCH biradical. In a MeCN:H$_2$O mixture, the ^{3}BCH biradical probably coexists with the triplet carbanion that has a pK_a of ca. 7.6 due to its acid–base equilibrium.[14] Therefore, the observation of the transient absorption at 514 nm in a water-rich solution which has a modest bathochromic shift compared with the band at 504 nm in acidic solutions may indicate the presence of the ^{3}BCH biradical coexisting with a moderate amount of the triplet carbanion.[22] In acidic solution, especially in a pH 0 solution, the intermediate observed should be predominantly due to the ^{3}BCH biradical. Some other studies[31,32] attribute the transient absorption at 520 nm maximum to the ^{3}BCH species based on ns-TA results for the photochemical reaction of KP with amino acids. When the transient absorption spectra are broad for the observed intermediate species, those intermediates with similar electronic structure often overlap with one another and can be difficult to precisely assign the intermediate by only using the transient absorption spectral results. However, vibrational spectroscopic methods including ns-TR^3 can provide fingerprint information for the intermediates involved in the photochemistry of the molecule of interest and can more easily distinguish those intermediates that have similar electronic structure. Therefore, based on the combined fs-TA and ns-TR^3 results for KP, we tentatively assign the intermediate with the transient absorption

around 324 and 500 nm to the ^{3}BCH species. Furthermore, the change of the kinetics at 496 nm is slower than that obtained at 524 nm. This directly implies that the new species generated by the decarboxylation reaction has a contribution to the transient absorption at 496 nm. A global fit of the fs-TA transient absorption obtained in a pH 0 acidic solution can extract a 8.7 ps time constant for ISC and a 1.73 ns time constant for the decarboxylation reaction. As shown in Figure 5, the resonance

Figure 5. Comparison of the ns-TR^3 spectrum obtained at 5 ns (A) and the DFT predicted Raman spectrum of the ^{3}BCH biradical (B). Below is the transient absorption of the ^{3}BCH biradical at 3.2 ns obtained in a MeCN:H$_2$O (1:1, pH 0) solution (C).

Raman spectrum at 5 ns collected in the acidic MeCN:H$_2$O (1:1, pH 0) solution presents a satisfactory agreement with the DFT calculation predicted Raman spectrum of the ^{3}BCH biradical, and this indicates that the intermediate detected at about 5 ns is the ^{3}BCH biradical. Hence, the triplet-mediated decarboxylation reaction of ^{3}KP takes place in the acidic solutions as well as in the water-rich solutions examined here.

Recent ab initio calculations predicted that the excited singlet and triplet states of the KP$^-$ anion were located within a few kcal/mol in energy.[20] This could explain the very high quantum yield observation for the ISC and the formation of triplet state KP. KP has a pK_a of 4.7; therefore, the KP$^-$ anion is the predominant form in the MeCN:PBS (1:1) solution (pH 7.4). A resonance Raman study on the ground state of KP in MeCN:PBS (1:1) solution also found that KP existed mainly as the KP$^-$ anion form (see Figure 9S, Supporting Information). Therefore, the photochemistry of KP in the MeCN:PBS (1:1) solution should be mainly determined by the excitation of the KP$^-$ anion. Figure 6 shows that the singlet excited state KP$^-$ anion has its maximum absorption at 335 nm and a weak broad absorption at 570 nm, which is almost the same as that observed in pure MeCN for the neutral form KP. The ca. 8.8 ps ISC time constant is associated with the singlet excited state directly transforming into the triplet state KP$^-$ anion (^{3}KP$^-$) that has two transient absorptions around 327 and 524 nm. After 40 ps, the consumption of the absorption at 524 nm is accompanied by an emergence of a broad transient absorption with maxima at 590 nm, and this transient absorption is very much like the characteristic absorption of the KP carbanion at
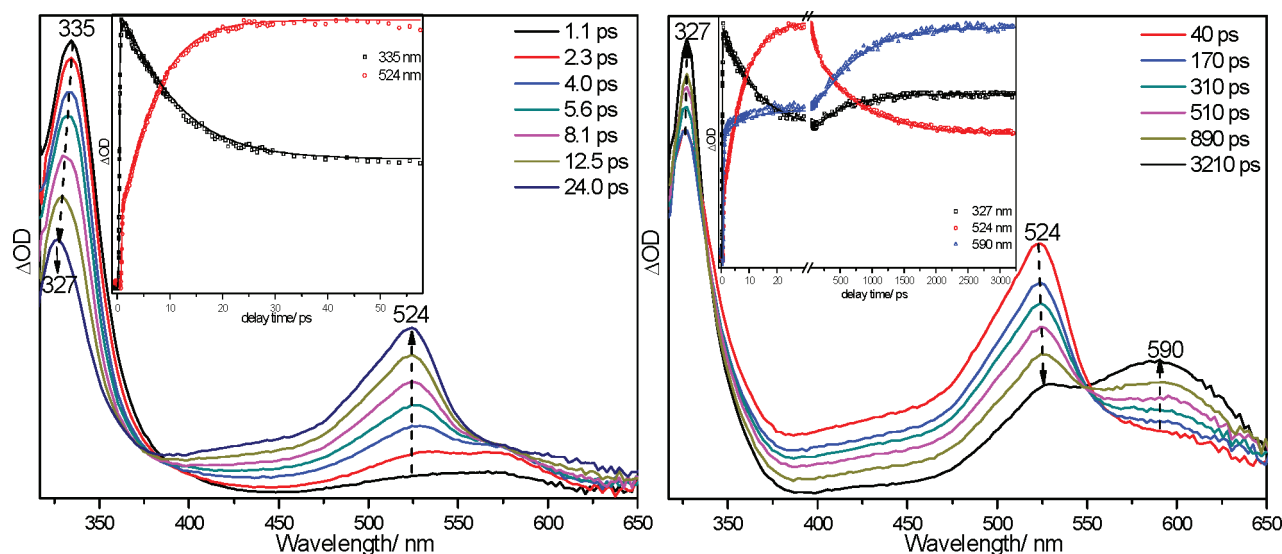
Figure 6. Transient absorption spectra of KP at early (left) and late (right) picosecond times recorded with 267 nm excitation in a MeCN:PBS (1:1) solution. The insets are the normalized kinetics recorded at maximum absorption peaks.

Scheme 1. Proposed Decarboxylation Reaction Mechanism of KP in the Water-Rich, Acidic, and PBS Solutions
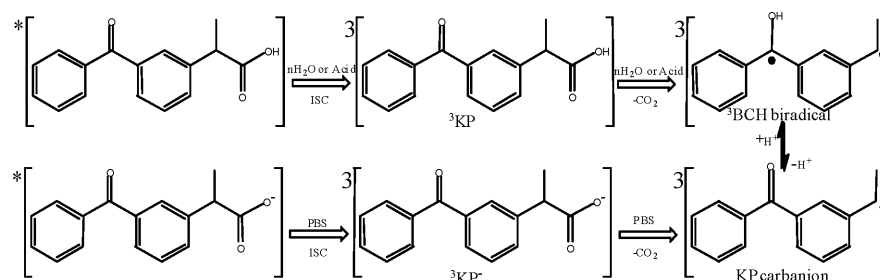
600 nm detected in water by previous LFP experiments.[33] Therefore, the new maximum absorption at 590 nm corresponds to the formation of the KP carbanion with a triplet state character. This is coincident with the results that the $^3KP^-$ species has not been detected in the ns-TR^3 experiment of KP in PBS solution and only a ^3BCH biradical (resonant structure of the triplet state KP carbanion) is observed in the resolution of ns-TR^3 experiments. The isosbestic point at 550 nm directly demonstrates that the $^3KP^-$ anion is the precursor of the KP carbanion. The time profiles of the absorbance changes at 524 and 590 nm are given in the insets of Figure 6 (right). Both the increasing and decreasing kinetics are described well by an exponential function with a lifetime of about 568 ps (see kinetics in Figure 6 (right)). Consequently, the decarboxylation reaction of KP in PBS solution is also directly initiated by the $^3KP^-$ anion and this is consistent with the issue that decarboxylation reactions are well-known to occur for a number of carboxylic acid triplet states.[34]

In conclusion, Scheme 1 depicts the proposed mechanism of KP irradiated by 267 nm in the water-rich, acidic, and PBS solutions. In the neutral water-rich or acidic solutions, the decarboxylation reaction of KP is initiated by the neutral form KP with the assistance of water or acid and occurs relatively slowly compared to the anion form of KP. A ^3BCH biradical intermediate is directly generated after the decarboxylation reaction of ^3KP. In PBS solution, the $^3KP^-$ anion mediates the decarboxylation reaction and generates the KP carbanion with a

triplet nature (this carbanion has a lifetime of about 200 ns[13−15,26]) and its resonant structure ^3BCH biradical would prevail due to the protonation of the KP carbanion in PBS solutions. Given the recent interest in the phototoxicity of KP and its use as a platform for developing phototriggers, the elucidation of the decarboxylation mechanisms of the neutral and anion forms of KP should prove to be useful in future work developing KP derivatives for various applications. It is interesting to note that some aromatic carbonyl phototriggers based on benzoin such as benzoindiethylphosphate (BDP) have a faster ISC of about 1−2 ps to form the triplet state that then undergoes deprotection on the nanosecond time scale,[35] but the related dimethoxybenzoin diethylphosphate (DMBDP) phototrigger does not have discernible ISC to form an analogous triplet state and proceeds via a singlet state pathway due to a bichromophoric interaction and then undergoes deprotection about 10 times faster with a quantum yield more than 2 times higher than BDP.[36] Since the aromatic carbonyl ISC in KP (about 10 ps) is much slower than in benzoin compounds like BDP (1−2 ps), it appears there could be greater room for using varying substituents to influence the reaction pathways and outcomes for KP based phototriggers as well as to influence the photoxicity in KP derivatives.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The fs-TA spectra of KP in the 10%, 50% water concentration solutions and acidic solutions, experimental procedures,

description of the fs-TA, ns-TR^3 instruments, and DFT calculations. 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

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