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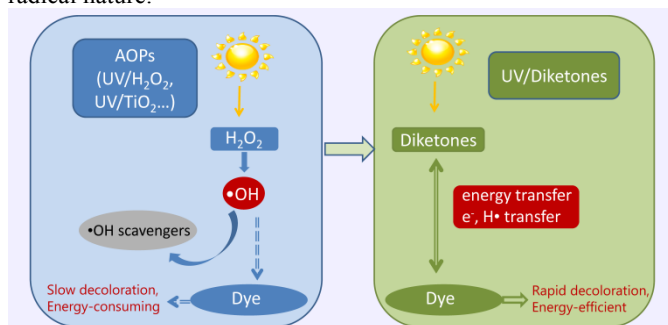
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The UV/diketone processes could degrade dyes faster and more selectively than the UV/H<sub>2</sub>O<sub>2</sub> process, due to their non-hydroxyl radical nature.



# Non-Hydroxyl Radical Mediated Photochemical Processes for Dye Degradation

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Xitong Liu, Xiaojie Song, Shujuan Zhang\*, Mengshu Wang and Bingcai Pan

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Using solar energy for the decontamination of wastewater is a promising solution to the water-energy nexus. Current advanced oxidation processes have unsatisfactory efficiency in the treatment of dye wastewaters due to the non-selectivity of hydroxyl radicals. More efficient photochemical approaches for dye degradation are highly needed. Three diketones, biacetyl, acetylacetone, and acetonylacetone, were proven to be potent activators for the photodecoloration of azo, triarylmethane and anthraquinone dyes. The photodegradation kinetics of Acid Orange 7 in the UV/diketone processes was much faster than that in the UV/H<sub>2</sub>O<sub>2</sub> system. Photoinduced energy and electron transfer were possible mechanisms for dye degradation in the diketone systems. Adducts of dye and acetylacetone were identified, indicating a unique dye degradation route through adduct formation and decomposition. Unlike acting only as the target substrate of •OH in advanced oxidation processes, dyes played vital roles in the UV/diketone processes. The findings here provide new insights for designing more efficient technologies for environmental remediation based on diketone photochemistry.

## 1. Introduction

Dye effluents from textile, paper and pulp, and tannery industries have become a great concern in modern society.<sup>1</sup> With the high demand for color fastness on textile, synthetic dyes are usually very resistant toward photo-bleaching. Without sufficient treatment, the released dyes will remain in the environment for a long time, posing a big threat to human health and ecosystems.

Quite a few methods, such as adsorption,<sup>2</sup> membrane filtration,<sup>3</sup> and chemical oxidation<sup>4</sup> have been proposed for the

decoloration of dye-laden wastewater. Due to the high oxidation and mineralization efficiency, advanced oxidation processes (AOPs) have attracted extensive research interests in the degradation of organic pollutants. In most AOPs, hydroxyl radical (•OH), with a high oxidation potential of 2.8 V, is generated and acts as the main oxidizing agent to destroy and mineralize the recalcitrant organic chemicals. Some well-known •OH based AOPs, including Fenton reactions, UV/H<sub>2</sub>O<sub>2</sub>, and UV/TiO<sub>2</sub> systems, have found applications in dye wastewater treatment.<sup>5-9</sup> However, since •OH can react with almost all organic moieties and many inorganic species at diffusion-controlled rates,<sup>10</sup> the coexisting matters in dye wastewater compete with dyes for •OH, leading to a relatively low decoloration efficiency when it comes to the treatment of real dye wastewater. Moreover, dyes often act as inner filters due to their high extinction coefficients in photochemical based AOPs (PAOPs).<sup>11, 12</sup> Therefore, the decoloration efficiency of PAOPs was often unsatisfactory at high concentration of dyes. It is still an urgent task to develop highly efficient decoloration technologies.

Using organic activators to degrade organic contaminants is another avenue in photochemical processes.<sup>13, 14</sup> It is reported

*State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing, 210023, P.R. China*

*Email: sjzhang@nju.edu.cn*

† Electronic Supplementary Information (ESI) available: Degradation products of AO7 and MO in the UV/diketone and UV/H<sub>2</sub>O<sub>2</sub> processes, mobile phase gradient for the LC-MS/MS experiments, the toxicology of the three diketones and H<sub>2</sub>O<sub>2</sub>, decoloration of MO, AR and RB in the UV/diketone and UV/H<sub>2</sub>O<sub>2</sub> processes, effect of solution pH and ethanol on the degradation of AO7 in the UV/diketone and UV/H<sub>2</sub>O<sub>2</sub> processes, and UV-Vis spectra of AO7 and diketones. See DOI: 10.1039/b000000x/

that natural organic matter can promote the degradation of pollutants in natural water through photosensitization.<sup>15,16</sup> Chu et al. utilized acetone as a photosensitizer to promote the degradation of disperse dyes.<sup>17,18</sup> Upon UV irradiation, energy could be transferred from triplet acetone to dye molecules through collision, leading to the decay of dyes. However, the use of acetone as a co-solvent makes the process expensive when it comes to the treatment of water-soluble dyes. Neevel et al.<sup>19,20</sup> used biacetyl (2,3-butanedione, denoted as BD) as a model substrate to investigate the light fastness of azo dyes, and observed a fast dye photodegradation in BD solutions. In Neevel's study, all azo dyes have OH group, leading to a high ratio of hydrazone isomers. They attributed the degradation of dyes to the oxidation by the adduct of O<sub>2</sub> with the triplet BD and acetyl radicals, as well as the hydrogen abstraction from -N-N- bond of hydrazones by the adduct of O<sub>2</sub> and BD.<sup>20</sup> This gave us a hint to utilize BD and its structural analogues as photo-activators for the degradation of organic dyes.

Acetylacetone (2,4-pentanedione, denoted as AA) and acetonylacetone (2,5-hexanedione, denoted as HD) belong to  $\beta$  and  $\gamma$ -diketones, respectively. They are similar to BD ( $\alpha$ -diketone) in chemical structure, but differ in several aspects, such as bond dissociation energy (BDE) and excitation energy. When applied in dye degradation, the three diketones acted differently.<sup>21</sup> The formation of charge-transfer complexes between dyes and diketones was proposed as the key step in the AA-mediated photochemical processes.<sup>21</sup> However, it is still unclear how the complexes are formed and whether these processes are efficient for other dyes. Moreover, the origins of the different behaviors of the three diketones in dye degradation were not fully elucidated. In this study, the three diketones, BD, AA, and HD, were investigated side-by-side as photo-activators for the decoloration of azo, triarylmethane, and anthraquinone dyes (Scheme S1). As a well-established AOP, the UV/H<sub>2</sub>O<sub>2</sub> process was employed as a reference system. The degradation products of dyes were analyzed, and the reaction mechanisms were elucidated with the aid of density functional theory (DFT) calculations.<sup>22,23</sup> This study may provide an entry point for the development of a novel type of environmental UV technologies based on the use of diketones as photo-activators, as well as an example to utilize DFT in environmental-remediation technologies.

## 2. Experimental Section

### 2.1 Materials

Acid Orange 7 (AO7), Methyl Orange (MO), Rhodamine B (RB), acetone, AA, BD, HD, H<sub>2</sub>O<sub>2</sub>, NaAc, HAc, phenol, chlorobenzene and ethanol were all of analytical grade and purchased from Shanghai Reagent Station, China. Alizarin Red (AR) was chemical grade. Methanol and formic acid used in LC-MS/MS experiments were of HPLC grade. Deionized water with a resistivity of 18.25 M $\Omega$  was used in all of the experiments.

### 2.2 Irradiation experiments

Irradiation experiments were carried out in a merry-go-round photoreactor (Nanjing StoneTech Electric Equipment Co., China, Scheme S2) with a 300 W medium-pressure mercury lamp (Shanghai Hongguang Tungsten & Molybdenum Technology Co., Ltd.). The light spectrum of this lamp is shown in Fig. S1. Water flowed in a jacket outside the lamp for cooling. Nine quartz tubes were arranged in a sample holder around the lamp. The tubes have an inner diameter of 2 cm and a length of 12 cm with a 25 mL volume. The distance between the lamp and the sample tube was 5 cm. During irradiation, the tubes rotate around the lamp with the sample holder and simultaneously self-rotate. The light intensity reaching the solutions was measured using a radiometer (Photoelectric Instrument Factory of Beijing Normal University, China) equipped with a sensor with peak sensitivity at 365 nm. The light intensity used in this work was in the range of 2.9 - 7.1 mW cm<sup>-2</sup>. More details about the light source was reported previously.<sup>21</sup> For decoloration kinetics, the experiments were conducted in duplicates. The relative standard deviation of the decoloration rate constant was less than 5%.

During irradiation, 25 mL solutions containing dyes and activators (AA, BD, HD or H<sub>2</sub>O<sub>2</sub>) were exposed to irradiation. The initial concentration of AO7, MO, AR and RB were 0.16, 0.12, 0.1 and 0.03 (or 0.05) mM, respectively. The initial dose of activators ([Activator]) was 0.5 or 1.0 mM. At certain time intervals after UV irradiation, UV-Vis spectra and absorbance at the characteristic absorption wavelengths of corresponding dyes were recorded using a UV-Vis spectrophotometer (UV-2550, Shimadzu Co., Japan).

### 2.3 LC-MS/MS experiments

LC-MS/MS analysis was carried out with a Thermo LCQ Advantage MAX LC-MS system through an ESI interface. The injection volume was 10  $\mu$ L. The scan type for mass was Full with a mass range of 50-1000 in a negative polarity mode (45% normalized collision energy). An Agilent Eclipse Plus C18 column (150 mm  $\times$  4.6 mm, 5 $\mu$ m) was used for LC-MS separation with gradient elution procedures, as shown in Table S1.

### 2.4 Laser flash photolysis (LFP)

LFP technique was employed to characterize the transient species in the photodegradation process. LFP experiments were performed using a Nd:YAG laser, which provided 355 nm pulses with duration of 5 ns. Samples for photolysis experiments were all bubbled with high-purity N<sub>2</sub> for 20 min before use. Detailed description of the LFP facilities can be found elsewhere.<sup>24</sup>

### 2.5 Computational methods

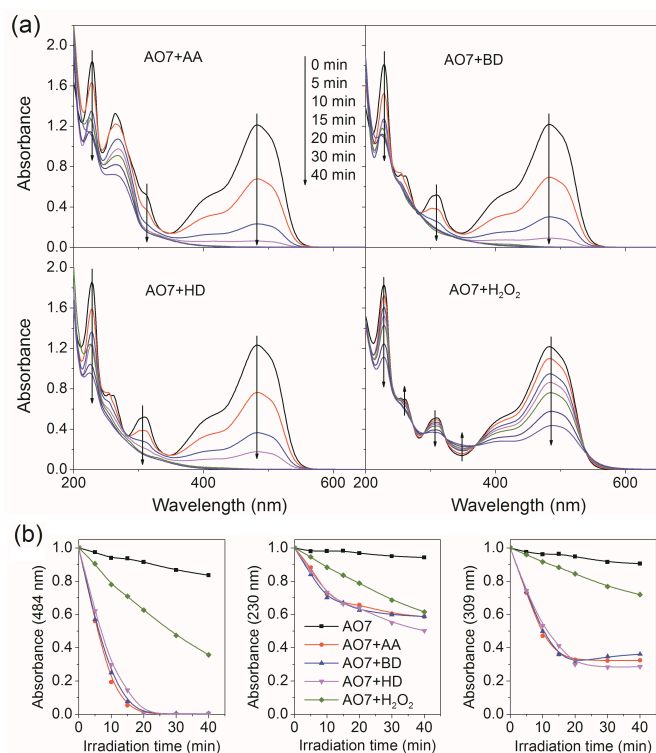
Calculations were performed using the Gaussian 03 software package.<sup>25</sup> Optimizations were performed at the B3LYP/6-311+G(d,p) level of theory followed by frequency calculations to verify that the stationary points obtained were true minima. Time-dependent density functional theory (TDDFT) was employed to calculate the excitation energy. Calculations on the open shell species were performed using the spin-unrestricted formalism. The solvent effect of water was considered based on the self-consistent-reaction-field (SCRF) method using the

integral equation formalism polarized continuum model (IEFPCM).<sup>26</sup> The electron accepting ability and electron donating ability were evaluated using the vertical electron affinity (VEA) and vertical ionization energy (VIE), respectively. VEA and VIE for excited state molecules were calculated by Eqs.1 and 2, respectively.<sup>27</sup>

$$\text{VIE}_{\text{S}_1} = \text{VIE}_{\text{S}_0} - E_{\text{S}_1}, \text{VIE}_{\text{T}_1} = \text{VIE}_{\text{S}_0} - E_{\text{T}_1} \quad (1)$$

$$\text{VEA}_{\text{S}_1} = \text{VEA}_{\text{S}_0} - E_{\text{S}_1}, \text{VEA}_{\text{T}_1} = \text{VEA}_{\text{S}_0} - E_{\text{T}_1} \quad (2)$$

### 3. Results and Discussion



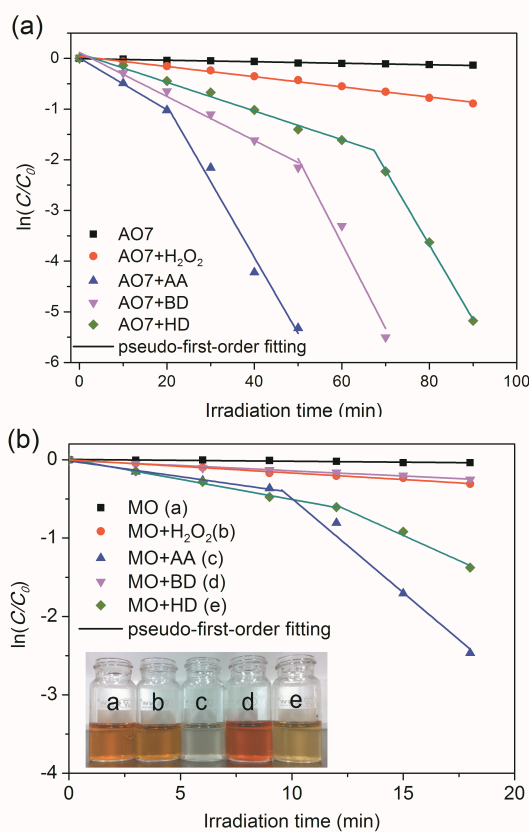
**Fig. 1** (a) Evolution of the UV-Vis spectra of AO7 in the UV/diketone and UV/H<sub>2</sub>O<sub>2</sub> processes. (b) Normalized intensities of the three main UV/Vis absorption peaks of AO7 plotted as a function of irradiation time. [AO7] = 0.16 mM, [Activator] = 1 mM. Light intensity: 7.0 mW cm<sup>-2</sup>. Samples were diluted for 2.5 times prior to analysis.

The decoloration performance of the UV/diketone processes were compared with the well-established UV/H<sub>2</sub>O<sub>2</sub> process. Fig. 1a shows the evolution of the UV-Vis spectra of AO7 in UV irradiated diketone and H<sub>2</sub>O<sub>2</sub> solutions. The peaks at 484, 230 and 309 nm correspond to the azo bond, the benzene and naphthalene moieties, respectively.<sup>28</sup> The three peaks diminished with prolonged irradiation in the UV/diketone processes, indicating the simultaneous destruction of azo linkage as well as the benzene and naphthalene rings of AO7. Thus, AO7 was effectively degraded in the UV/diketone processes, not only just decolorized. (Note that acetone at the same dose was ineffective for the decoloration of AO7 under otherwise identical conditions.)<sup>21</sup> The degradation products of AO7 were shown in Table S2. In the UV/H<sub>2</sub>O<sub>2</sub> process, besides

the decrease of the three absorption peaks, the absorption at 350 nm was increased during irradiation, attributed to the formation of hydroxylated intermediates. This phenomenon was also observed in Fe<sup>III</sup>-TAML-catalyzed oxidation of AO7.<sup>29</sup> In comparison, the decoloration of AO7 in the UV/diketone processes was much more complete.

The decline of the three characteristic peaks of AO7 in the four processes is compared in Fig. 1b. The cleavage of the azo bond was much faster in the UV/diketone processes than that in the UV/H<sub>2</sub>O<sub>2</sub> process. For the destruction of benzene and naphthalene rings, the UV/diketone processes were also advantageous over the UV/H<sub>2</sub>O<sub>2</sub> process at the initial stage. Upon complete decoloration, 70% of the naphthalene rings and 40% of the benzene rings were destroyed in the UV/diketone processes.

AA and HD were also more efficient than H<sub>2</sub>O<sub>2</sub> in destroying the azo linkage of MO, as proved by the rapid disappearance of the absorption peak at 464 nm (Fig. S2). BD was not very effective in decolorizing MO. Moreover, after irradiated in BD solutions, the maximum absorption peak of MO shifted to a longer wavelength, indicating the formation of colored intermediates or an enhancement of the delocalization of the conjugated electrons in the MO molecules. This phenomenon suggests that the mechanisms in the UV/BD and UV/AA (HD) processes might differ in some aspects.

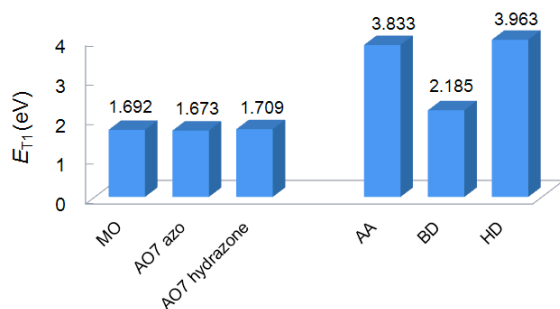


**Fig. 2** Degradation kinetics of AO7 (a) and MO (b) in the UV/diketone and UV/H<sub>2</sub>O<sub>2</sub> processes. [AO7] = 0.16 mM, [MO] = 0.12 mM, [Activator] = 1 mM, light intensity: (a) 2.9 mW cm<sup>-2</sup> (b) 7.1 mW cm<sup>-2</sup>.



The degradation of azo dyes in the UV processes could be described with the pseudo first-order kinetic model. According to Fig. 2a, all the three diketones exhibited much faster decoloration kinetics toward AO7 than the UV/H<sub>2</sub>O<sub>2</sub> process. The most efficient one was the UV/AA process. All the three diketone systems showed somewhat two-stage decoloration kinetics, while the dye degradation in the UV/H<sub>2</sub>O<sub>2</sub> process kept at a constant rate. The observed pseudo-first order decoloration rate constant ( $k_{\text{obs}}$ ) of AO7 in the UV/AA, UV/BD and UV/HD processes were 4.1, 3.3, 1.8 times higher than that in the UV/H<sub>2</sub>O<sub>2</sub> process, respectively. At the second stage, the ratio of  $k_{\text{obs}}$  increased to larger than 13.0. Thus, the UV/diketone processes were much more advantageous than the UV/H<sub>2</sub>O<sub>2</sub> process for AO7 decoloration. Similar results were observed for the other two types of dyes, RB (a triarylmethane dye) and AR (an anthraquinone dye), as illustrated in Figs. S3 and S4.

The self-acceleration phenomenon was also observed in the decoloration of RB by the UV/AA and UV/HD processes (Fig. S3). Although the photodecoloration rates of RB by AA and HD were initially slower than that by H<sub>2</sub>O<sub>2</sub>, they turned faster and exceeded that in the H<sub>2</sub>O<sub>2</sub> system. For the decoloration of MO, the UV/AA and the UV/HD processes were also faster than the UV/H<sub>2</sub>O<sub>2</sub> process, but the UV/BD process failed to decolorize MO as shown by the deepened color after irradiation (Fig. 2b). These results suggest that an investigation of the quantitative structure-activity relationship is necessary to understand the decoloration of variant dyes in the different photochemical processes.

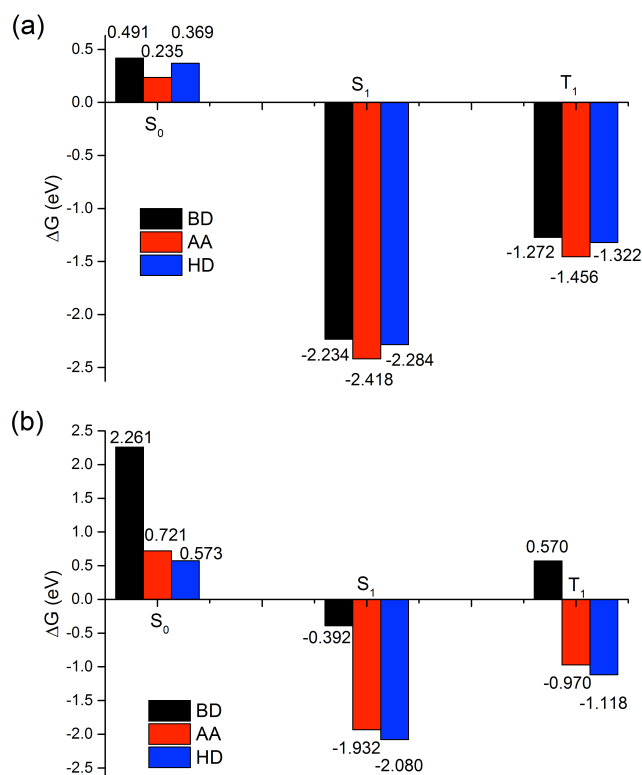


**Fig. 3** Triplet excitation energy ( $E_{T1}$ ) of dyes and diketones calculated by DFT.

The two-stage kinetics of photodecoloration of AO7, as well as MO and RB, may be attributed to the change of pH during the photodegradation of dyes.<sup>21</sup> With the progress of the decoloration reaction, the pH of the dye solutions was decreased from ca. 6 to 4-5. By controlling the solution pH with NaAc/HAc buffer solutions, the three UV/diketone processes showed larger initial pseudo-first order decoloration rate constants at pH 4.0 than at pH 5.8 (Fig. S5), while the rate constant was not significantly altered in the UV/H<sub>2</sub>O<sub>2</sub> process. A larger decoloration rate at a lower solution pH is meaningful in practical applications, since the degradation of dyes was always accompanied by the decrease in solution pH due to the formation of acidic intermediates. Faster decoloration in acidic

environment is beneficial to the complete decoloration of dye pollutants.

The high efficiency of diketones in dye degradation as well as the different behaviors of the three diketones provides the impetus to investigate the underlying mechanisms. The decoloration effectiveness of the UV/diketone processes was free from the interference of alcohol (Fig. S6), suggesting a unique decoloration mechanism without the involvement of non-selective hydroxyl radicals. The non-hydroxyl radical mediated mechanism was further confirmed by the electron paramagnetic resonance experiments with DMPO as the spin trap for  $\cdot\text{OH}$ .<sup>21</sup> No evident radicals were trapped in irradiated AA and HD solutions, while in BD solution a six-line signal was detected, which corresponds to a DMPO-CH<sub>3</sub>CO $\cdot$  adduct.<sup>21</sup> The difference in the amount of generated acetyl radicals may be attributed to the different BDEs of the three diketones. According to the DFT calculation, the BDE of BD (3.02 eV, consistent to the reported value of 3.01 eV<sup>19,30</sup>) was lower than those of AA and HD (3.90 and 3.92 eV, respectively), thus more prone to dissociation to CH<sub>3</sub>CO $\cdot$ . In the UV/BD process, CH<sub>3</sub>CO $\cdot$  either take part in the degradation of dyes directly or by forming adduct with molecular oxygen as suggested by Neevel et al.<sup>19</sup> In the UV/AA and UV/HD processes, CH<sub>3</sub>CO $\cdot$  might be less important due to its relative scarcity.<sup>21</sup>

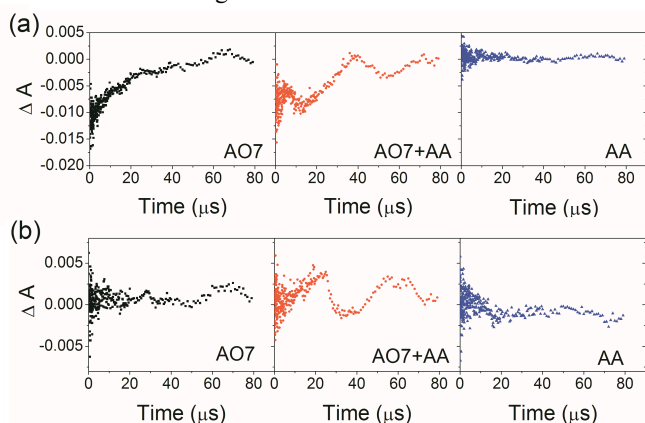


**Fig. 4** Change of Gibbs free energy during electron transfer between different states of MO (shown in x-axis) and triplet states of diketones calculated by DFT. (a) Electron transfer from MO to diketones, (b) Electron transfer from diketones to MO. Positive values of  $\Delta G$  suggest that electron transfer could not happen, and negative values of  $\Delta G$  suggest that electron transfer could happen spontaneously.

In the UV/AA and UV/HD processes, although formation of free radicals was not evident, the degradation of dyes was very rapid, possibly due to several mechanisms. It has been reported that photo-induced energy and electron transfer could happen between dyes and ketones.<sup>31</sup> In Chu et al.'s work, energy transfer from triplet acetone to dye was considered to be the main mechanism responsible for dye degradation.<sup>17, 18</sup>

The possibility of energy transfer between dyes and the diketones was evaluated through DFT calculation. It is known that dyes, like AO7, has very low triplet quantum yield (ca.  $10^{-3}$ ) under light irradiation.<sup>32</sup> The triplet excitation energies of the three diketones were higher than that of dyes (Fig. 3). Thus, energy transfer from the triplet diketones to the ground state dyes could occur in the presence of diketones upon UV irradiation, increasing the amount of triplet dyes. Triplets were more reactive due to the longer lifetimes and the presence of unpaired valence electrons, thus dyes would be more prone to degradation.

Using similar approach, the possibility of electron transfer in the UV/diketone processes was evaluated by the change of Gibbs free energy ( $\Delta G$ ) in the electron transfer between diketones and dyes. The results demonstrate that electron transfer between ground-state dyes and triplet diketones could not happen, while electron transfer between excited dyes and triplet diketones were spontaneous (Fig. 4). After electron transfer, anion and cation radicals of dyes were produced and underwent further degradation.

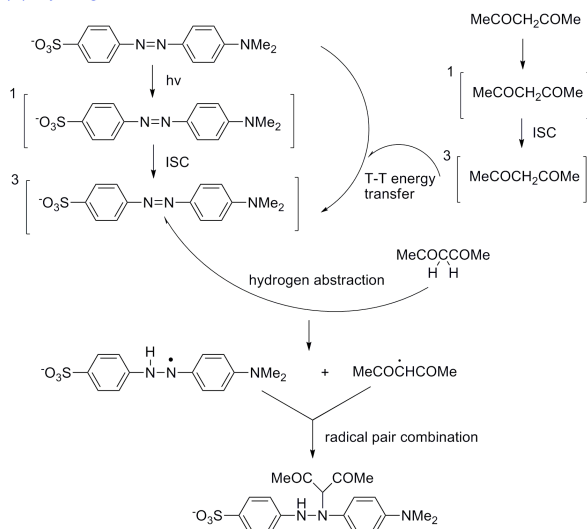


**Fig. 5** (a) Transient absorption at 480 nm in LFP experiment. (b) Transient absorption at 550 nm in LFP experiment.

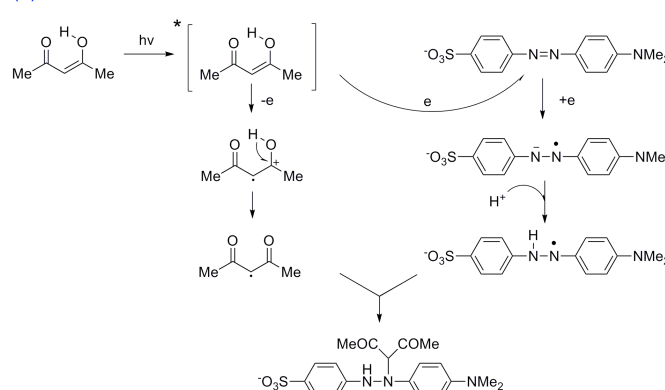
The electron transfer between AO7 and AA were further proved in laser flash photolysis (LFP) study. The main feature of the laser induced spectral change of AO7 was the photo-bleaching of the band around 480 nm (see Fig. 5a), which was indicative of the depletion of the ground states and the formation of excited states.<sup>32</sup> The kinetics of AO7 bleaching recovery was different in the presence of AA. A second-phase bleaching occurred and reached maximum in ca. 55 ms. In Fig. 5b, the absorption peak at 550 nm in the AO7-AA sample could be a signal of  $\text{AO7}^{+\bullet}$ , according to Vinodgopal et al.<sup>32</sup> The second peak occurred at 55 ms, matched exactly in the AO7 re-bleaching phase in the AO7-AA sample in Fig. 5a, indicating

the simultaneous depletion of the ground state AO7 and the generation of  $\text{AO7}^{+\bullet}$ . The generation of  $\text{AO7}^{+\bullet}$  could be induced by the electron transfer from the excited dyes to the triplet AA, which is supported by the DFT results.

#### (a) Hydrogen abstraction



#### (b) Photoinduced electron transfer

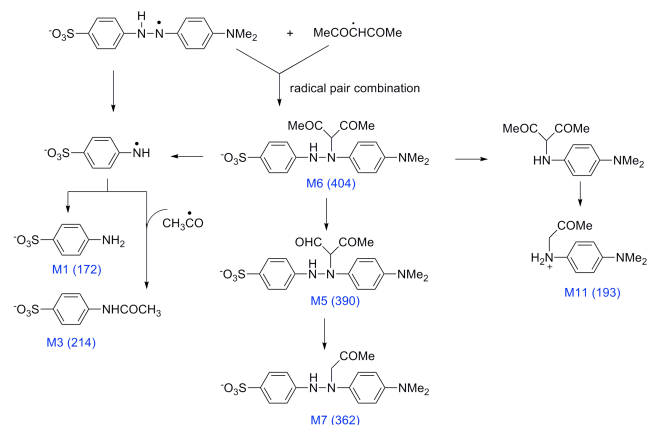


**Scheme 1.** Possible routes for the formation of the molecular adduct of MO and AA.

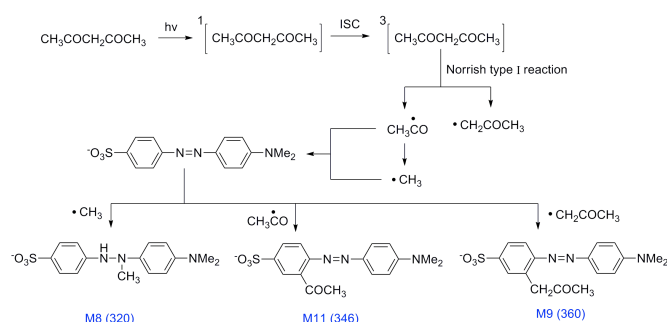
Besides energy and electron transfer, hydrogen transfer could also happen in the dye/diketone systems. In LC-MS/MS experiment, molecular adducts of AO7-AA and MO-AA were observed (with  $m/z$  values of 427 and 404, respectively, see Tables S1 and S2). We infer that these adducts are important for dye degradation in the UV/AA process. The possible formation routes for the MO-AA adduct are presented in Scheme 1. The triplet state of MO abstracts a hydrogen atom from the central carbon of AA, generating two radicals. Then the radicals undergo radical pair combination, yielding a molecule adduct. Note that the hydrogen transfer process could not easily happen in solutions due to the high reactivity of hydrogen atom ( $\text{H}\cdot$ ). It is possible that AA and MO form a triplet complex, and the hydrogen abstraction occurs within the complex. AA and MO at ground state did not form complex, indicating by the fact that the UV-Vis spectra of MO-AA

solutions were exactly the sum of the spectra of individual AA and MO solutions (Fig. S7). In excited state, however, due to the increase of both electron donor and acceptor abilities, “exciplex” could be formed and facilitate the electron transfer reaction within the complex.<sup>33</sup> Similar hydrogen transfer reaction in triplet complex of ketone and phenol has been reported.<sup>34</sup> In another possible route, the excited enol form of AA transfer an electron to the MO molecule, also leading to the formation of adduct through some sequential transformations.

#### (1) Molecule adduct dissociation



#### (2) Radical addition



**Scheme 2.** Proposed reaction routes in the UV irradiated MO-AA system.

The two possible degradation routes of MO in the UV/AA process are presented in Scheme 2 based on LC-MS/MS analysis. One route is the dissociation of the MO-AA adduct, leading to products M1, M3, M5, M6, M7, M11 (Table S2). Another route is the reaction between MO molecule and carbon centered radicals generated from the decomposition of excited AA. Oxygen may also combine with carbon centered radicals, forming peroxy radicals.<sup>19</sup> These radicals can add to benzene ring or to the  $-N=N-$  bond, or initiate oxidative degradation. The formation of M2 could be a product of MO oxidation by peroxy radicals. The “simultaneous reduction and oxidation” is a uniqueness of the current diketone mediated dye degradation. It is possible that several mechanisms take effect simultaneously, leading to a rapid degradation of dyes. Note that the degradation products of MO in the UV/BD process were different from that in the UV/AA and UV/HD processes (Table S2). Due to the lack of the hydrogen abstraction route in

the UV/BD process, only carbon-centered radicals played the main role in dye degradation, leading to the relatively low degradation efficiency for different dyes.

Phytotoxicity study using rice seeds demonstrates that the toxicity of irradiated dye solutions was not increased after the UV/AA process.<sup>21</sup> According to the median lethal dose and lethal concentration, the hazardous level of AA is very close to that of  $H_2O_2$ , while the toxicity of BD and HD are much lower (Table S4). The main degradation products of the three diketones in the photochemical processes were formic acid and acetic acid,<sup>21</sup> which could be used as carbon source of microbes. Therefore, the high decoloration efficiency and the good biocompatibility make the UV/diketone processes suitable in real applications. For example, the UV/diketone processes could be used for dye decoloration and degradation followed by mineralization with other AOPs or biological treatment processes, providing an energy-efficient way to reduce the environmental impact of dyeing wastewater.

It is worth noting that although various kinds of dyes could be degraded rapidly in the presence of diketones, the degradation of colorless compounds like phenol and chlorobenzene was not significantly accelerated after adding diketones.<sup>21</sup> The UV/diketone processes provided much better decoloration performance than the UV/ $H_2O_2$  process, suggesting that the UV/diketone processes were more target-selective. When it comes to the treatment of real dye wastewater, the co-existing organic matters often suppress the decoloration efficiency in AOPs. The non-hydroxyl radical mechanism of diketone induced degradation of dyes would impart this method great practical significance in the treatment of real dye effluents with high content of co-existing matters.

## Conclusions

This study shows that two diketones, AA and HD, could decolorize azo, triarylmethane and anthraquinone dyes effectively under UV irradiation. The degradation kinetics of AO7 in the UV/diketone processes was much faster than that in the UV/ $H_2O_2$  process. The degradation of dyes in the UV/diketone processes was based on photo-induced energy transfer from triplet diketones to ground-state dyes, electron transfer between triplet diketones and excited dyes, and hydrogen transfer between diketones and dyes. These mechanisms were different from the  $\bullet OH$ -based AOPs. Consequently, the UV/diketone processes are suitable for the treatment of real dye wastewater with high efficiency and selectivity. For another diketone, BD, due to the lack of easily abstractable hydrogen atoms, acetyl radicals played the main role in dye degradation, which may be attributable to its restricted effectiveness for different dyes. The remarkable performance of the UV/AA process signifies a further study on the photochemistry of diketones in aqueous solutions and may pave the way for new methods derived from redox photochemistry of diketones.



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## Notes and references

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The UV/diketone processes could degrade dyes faster and more selectively than the UV/H<sub>2</sub>O<sub>2</sub> process, due to their non-hydroxyl radical nature.

