



Fate and implication of acetylacetone in photochemical processes for water treatment



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ABSTRACT

Acetylacetone (AA), due to the peculiar enol-keto structures, has attracted wide scientific interests. In terms of photo-decolorization, it works much more efficiently than the well-known H_2O_2 . However, there is very limited information on the photochemistry of AA in aqueous solutions. Herein, the photolysis kinetics, quantum yield, mass balance, decomposition pathway, and bioavailability of AA during UV irradiation were systematically investigated. It seems that photophysical processes predominated over photochemical ones when AA was irradiated with UV light. Although the quantum yield of AA (0.116) was much lower than that of H_2O_2 (1.0), the stronger light absorption of AA and the better overlap of the AA absorption spectrum with the solar emission spectrum, as well as the direct energy/electron transfer mechanisms, ensured its high efficiency in photochemical processes. The main degradation products of AA in photochemical processes were similar to the metabolic products in bio-fermentation. Besides, the irradiated AA solution showed a high bioavailability to the cells in activated sludge. Therefore, the UV/AA process might be a promising pre-treatment approach for bio-treatment. The results provide new insights into the photochemical fate and implication of β -diketones in aqueous solutions.

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1. Introduction

β -diketones and their derivatives are of great importance in many fields by virtue of a number of interesting and specific properties originating from their dicarbonyl structures (Urbaniak-Domagala, 2011; Verma et al., 2014). Acetylacetone (abbreviated as AA) is one of the simplest β -diketones. It has been widely used in organic synthesis as precursors or catalysts (metal complexes) and in chemical analysis due to its strong chelating ability (Zhou et al., 2008). AA is also served as an additive in gasoline, lubricants, inks, and dyes (Budavari et al., 2001). It is reported that the content of AA in one printing ink was as high as 6% (w/w) (Rastogi, 1991). Besides the direct release from various waste streams, AA was also a possible semi-oxidation product in water treatment, such as the ozonation of sludge-press liquors (Boyle and McCullough, 1996).

The crucial feature of AA is the keto-enol tautomerization. The population of keto and enol depends on many factors, such as the solvent polarity (Hammond et al., 1959), temperature (Burdett and

Rogers, 1966), and the presence of UV irradiation (Coussan et al., 2003; Veierov et al., 1973, 1977). For example, in aliphatic hydrocarbon solvents, including n-hexane, n-heptane, cyclohexane, and benzene, AA exists predominantly in the chelated enol (Veierov et al., 1977), while the keto form predominates in aqueous solutions due to the strong intermolecular hydrogen bonding with water (Hammond et al., 1959).

With structural similarities to relevant biomolecules and photochromic substances, in combination with its structural simplicity, AA is a prototypical candidate for a systematic study of the photoinduced processes (Verma et al., 2014). The basic photo-physical and photochemical processes of AA have been intensively investigated in gas phase (Zhou et al., 2008; Mayo and Takeshita, 1963; Yoon et al., 1999; Harrison and Lossing, 1959) and in isolated cryogenic matrices (Trivella et al., 2010). The photodynamics of AA, especially the photoisomerization and dissociation are the main focus points in these studies.

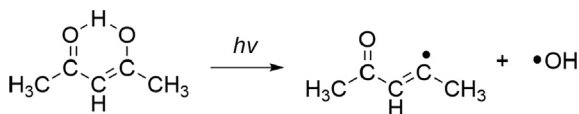
In the first report on the photochemical behavior of AA (Harrison and Lossing, 1959), a split into two radicals was proposed as the main decomposition pathway of AA by excited mercury in gas phase reactions.

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In another work (Yoon et al., 1999), OH radical was observed as a photo-fragment production of AA in gas phase due to the π - π^* transition of the enolic AA.



When AA was isolated in cryogenic matrices, photoisomerization was observed as the main process, while tautomerization and fragmentation remained limited (Trivella et al., 2010). The photoisomerization involves eight enolic AA stereoisomers, including seven nonchelated isomers and one chelated enol.

As compared to the intensive investigation in the gas phase and isolated matrices, the knowledge on the photochemistry of AA in liquid phase is very limited. The photoinduced conversion from chelated enol to nonchelated enol and then the thermal conversion of nonchelated enol to keto form (Scheme 1) were determined as the main photochemical behaviors of AA in nonpolar solvents (Veierov et al., 1977).

To the best of our knowledge, there is only very limited experimental information currently available in the peer-reviewed literature on the aqueous photochemistry of AA (Liu et al., 2014; Wang et al., 2013; Zhang et al., 2014; Wu et al., 2015). Our previous work has demonstrated that the UV/AA process was much more efficient than the OH radical-mediated UV/H₂O₂ process in terms of dye decolorization (Zhang et al., 2014). Interestingly, the production of $\cdot\text{OH}$ and acetyl radicals was negligible in the UV-irradiated AA solution with 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as the probing molecule for electron spin resonance (ESR) determination (Zhang et al., 2014). These results suggest that both the split pathway in Reaction 1 and the fragment pathway in Reaction 2 might be excluded as the predominant ones when AA was irradiated in aqueous solutions. To interpret the unexpectedly high efficiency of AA in the photobleaching of dyes, a photoinduced electron/energy transfer hypothesis was put forward based on both quantum chemical calculation and experimental analysis (Liu et al., 2014; Zhang et al., 2014). It should be noted that our previous work focused mainly on the roles of AA in the photodecomposition of dyes (Liu et al., 2014; Wang et al., 2013; Zhang et al., 2014). Little attention was paid to the fundamental photochemistry of AA itself. As a matter of fact, the knowledge of the photochemistry of AA in aqueous solutions and its fate in the photochemical processes is not only important to the potential application of the UV/AA process as a water pollution control

method but also necessary for us to better understand the photochemical behaviors of other β -diketones upon which the wide applicability of β -diketones is based. Therefore, the photochemistry of AA in aqueous solutions was systematically investigated in the present work. Based on the results, the environmental implication of AA was also discussed.

2. Material and methods

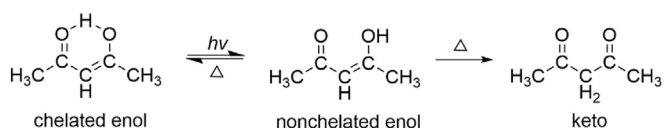
2.1. Materials

All chemicals were obtained from commercial source and used as received without further purification. AA (C₅H₈O₃), H₂O₂ (30% v/v), and formaldehyde (HCHO) of analytical purity grade were purchased from Shanghai Reagent Station, China. Acetaldehyde (CH₃CHO), lactic acid (C₃H₆O₃), KI, KIO₃, CuCl₂, Cu(ClO₄)₂, Fe(ClO₄)₃, Cr(ClO₄)₃, HClO₄, NaOH, NaCl, Na₂SO₄, NaNO₃, and NaHCO₃ of analytical purity grade were purchased from Nanjing Reagent Station, China. Acid Orange 7 (AO7, C₁₆H₁₁N₂OSO₃Na) was obtained from Sigma-Aldrich Co. Ltd., USA. DMPO of analytical purity grade was bought from J&K Co., China. Formic acid (HCOOH), acetic acid (CH₃COOH), pyruvic acid (C₃H₄O₃), and KOH of chromatography grade were purchased from Roe Scientific Inc., USA, Tedia Co. Inc., USA, Tokyo Chemical Industry Co. Ltd., Japan, and Sigma-Aldrich Co. Ltd., USA, respectively. Three natural organic matter (NOM) powders from Suwannee River (Product No. 1R101N), Upper Mississippi River (Product No. 1R110N), and Nordic Reservoir (Product No. 1R108N) were obtained from the International Humic Substances Society (<http://www.humicsubstances.org/index.html>) and were labeled as SR, UR, and NR, respectively. Ultrapure water was used for the preparation of sample solutions.

2.2. Irradiation experiments

Two photoreactors were used in the irradiation experiments. One is a rotating disk photoreactor (Nanjing StoneTech Electric Equipment Co., China) with a 300 W medium-pressure mercury lamp (MP-Hg, Shanghai Hongguang Tungsten & Molybdenum Technology Co., Ltd.) as the radiation source. More details about this photoreactor are available in a previous report (Liu et al., 2014). Another was a self-made cylindrical borosilicate glass reactor (600 mL) with a 10 W low-pressure mercury UV lamp (LP-Hg, GPH212T5L, Heraeus Noblelight) as the UV light source (Li et al., 2012). The MP-Hg lamp was polychromatic with main emissions at 254, 303, 313, 365, 405, 436, 546, and 578 nm whereas the LP-Hg lamp was monochromatic at 254 nm (Fig. S1).

It is reported that MP-Hg lamps are advantageous over LP-Hg lamps in providing cost-effective disinfection of water for large systems (Jin et al., 2006). MP-Hg lamps can produce much higher intensity than LP-Hg lamps. Therefore, fewer lamps may be needed for a certain flow. As a consequence, the use of MP UV systems might be helpful to reduce capital and maintenance costs (Marshall, 1999). However, the measurement of polychromatic UV is complicated. The traditional fluence measurement methods



Scheme 1. The photoinduced conversion of AA (Veierov et al., 1977).

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