Benzaldehyde-Promoted (Auto)Photocatalysis under Visible Light: Pitfalls and Opportunities in Photocatalytic H\textsubscript{2}O\textsubscript{2} Production

Igor Krivtsov\textsuperscript{a,b,*} Ashish Vazirani\textsuperscript{a} Dariusz Mitoraj\textsuperscript{a} Radim Beranek\textsuperscript{a,*}

\textsuperscript{a} Institute of Electrochemistry Ulm University, Albert-Einstein-Allee 47, 89081 Ulm, Germany
Igor Krivtsov, Ashish Vazirani, Dariusz Mitoraj, Radim Beranek

\textsuperscript{b} Department of Chemical and Environmental Engineering, University of Oviedo, 33006 Oviedo, Spain
Igor Krivtsov

*Corresponding authors: Igor Krivtsov (krivtsovigor@uniovi.es)
Radim Beranek (radim.beranek@uni-ulm.de)

Abstract
Selective photooxidation of aromatic alcohols to corresponding aldehydes is a widely used model reaction for evaluation of performance of heterogeneous photocatalysts. A chief example is the photocatalytic production of hydrogen peroxide via reduction of dioxygen with concomitant photooxidation of benzyl alcohol to benzaldehyde. Although it has long been known that photoexcitation of benzaldehyde under UV light yields reactive benzaldehyde radicals capable of oxidizing substrates such as benzyl alcohol, it was assumed that such autocatalytic processes cannot be initiated under visible light irradiation. Herein we demonstrate the ability of benzaldehyde to promote auto-photocatalytic oxidation of benzyl alcohol and produce large quantities of H\textsubscript{2}O\textsubscript{2} in solvent-free (no water) or biphasic (with water) systems even under nominally solar-simulated visible light (>420 nm cutoff filter) irradiation. While these results open up broader prospects for the use of benzaldehyde in visible light-driven photocatalysis as exemplified by the ability of benzaldehyde to photocatalyze H\textsubscript{2}O\textsubscript{2} production even in the presence of alternative electron donors (e.g., ethanol), they also shed some critical light on the plethora of research reports on photocatalytic H\textsubscript{2}O\textsubscript{2} production in which benzyl alcohol was employed as electron donor. Since the autocatalytic pathway based on the photocatalytic activity of benzaldehyde formed during photocatalysis under such conditions cannot be neglected, the interpretations of photocatalytic performance are likely contentious and distorted in such reports. We conclude that the use of benzyl alcohol as a model electron donor in photocatalytic studies should be definitely discouraged, and highlight the importance of carrying out simple check protocols for excluding similar issues when using alternative substrates.

Keywords: photocatalysis; hydrogen peroxide; benzyl alcohol; benzaldehyde; autocatalysis; visible light
Introduction

Heterogeneous photocatalysis represents a vibrant research field\(^1\) with possible applications ranging from water detoxification\(^4\) to solar fuel generation\(^5\) and chemical synthesis.\(^6\)\(^-\)\(^8\) Due to its simplicity, selective photooxidation of benzyl alcohols is often employed in photocatalysis as a model reaction for evaluation of the performance of various photocatalysts.\(^9\)\(^-\)\(^15\) A prominent example is the photocatalytic production of hydrogen peroxide, an attractive high-value compound that can be employed as a fuel or a versatile and non-toxic oxidizing agent in various industrial processes, via reduction of dioxygen with concomitant photooxidation of benzyl alcohol to benzaldehyde.\(^16\)\(^-\)\(^18\) As a rule, a blank test intended to confirm the photocatalytic nature of the reaction is performed by irradiating the solution of benzyl alcohol or other electron donor in the absence of photocatalyst, thus ruling out possible photochemical reactions which the substrate might undergo. This approach, however, does not take into account the photochemical behaviour of products of partial oxidation of aromatic alcohols that are produced during irradiation of the suspension of photocatalysts in the substrate solution. In 2016, the Augugliaro group reported the photocatalytic effect of ortho-methoxybenzaldehyde, produced by oxidation of ortho-methoxybenzyl alcohol over TiO\(_2\) photocatalysts, on homogeneous photooxidation of other alcohols under UV light.\(^19\) Surprisingly, this important finding that should have alarmed many researchers has been sadly neglected by the community, as this paper has received only few citations so far. Two years later, Pavan \textit{et al.} addressed the question of benzyl alcohol self-oxidation under UV-light.\(^20\) When irradiating benzyl alcohol solution in acetonitrile with UVA light, they observed that after a long induction time benzaldehyde was formed. The same experiments performed in the presence of a TiO\(_2\) photocatalyst showed that benzaldehyde was produced immediately upon starting irradiation; however, when the TiO\(_2\) photocatalysts was extracted after a certain time interval, the benzyl alcohol oxidation clearly proceeded further and the benzaldehyde concentration continued to grow. In other words, one can assume that the formed benzaldehyde initiated a photochemical reaction with benzyl alcohol leading to the oxidation of the latter according to the mechanism adapted from Bradshaw\(^21\), Heyes\(^22\) and Pavan\(^20\) and shown in Scheme 1. The current knowledge on photogeneration of radical species in benzaldehyde solutions was recently summarized in a review by Kokotos \textit{et al.}\(^23\) It was also observed that the UV-excited benzaldehyde triplet state can be effectively quenched by triplet-state energy acceptors,\(^24\) and when dissolved in a good hydrogen donor it can perform hydrogen abstraction leading to the formation \(\alpha\)-hydroxybenzyl radical in general,\(^25,\)\(^26\) or of diols in the presence of alcohols.\(^21\) Arcas \textit{et al.} provided further insight into the autooxidation processes in benzyl alcohol/benzaldehyde systems, claiming the formation of singlet oxygen being responsible for the oxidation of benzyl alcohol to benzaldehyde with concomitant
production of $\text{H}_2\text{O}_2$ under UV light.\textsuperscript{27} However, it was not clear which species was responsible for the formation of singlet oxygen. Notably, the studies of Pavan \textit{et al.}\textsuperscript{20} and Arcas \textit{et al.}\textsuperscript{27} concluded that the so-called autooxidation of benzyl alcohol occurs only under UV-light and that it is completely inhibited already at 405 nm.\textsuperscript{20}

An illustrative example that alerted our suspicion that the peculiar photochemistry of benzaldehyde might have a significant, yet unrecognized, effect on estimation of photocatalytic $\text{H}_2\text{O}_2$ production when using benzyl alcohol as electron donor can be found in a recent paper by Yamashita \textit{et al.}\textsuperscript{28} The authors reported enhanced photocatalytic $\text{H}_2\text{O}_2$ production under visible light ($\lambda > 420$ nm) using a hydrophobic Ti-based metal-organic framework (MOF) photocatalyst in a biphasic system of benzyl alcohol and water without any additional organic solvent. As the produced $\text{H}_2\text{O}_2$ was immediately extracted into the water phase and did not undergo decomposition at the photocatalyst suspended in the organic (benzyl alcohol) phase, this system allowed obtaining relatively high concentrations of $\text{H}_2\text{O}_2$. Nevertheless, the profiles of the $\text{H}_2\text{O}_2$ evolution reported by Yamashita \textit{et al.}\textsuperscript{28} clearly suggest that an autocatalytic mechanism might be at play since the $\text{H}_2\text{O}_2$ production was accelerated after certain irradiation time.\textsuperscript{28} This prompted us to investigate the issue of benzaldehyde-mediated auto-photocatalysis in $\text{H}_2\text{O}_2$ production systems in detail. Herein, we provide a conclusive evidence for the ability of benzaldehyde to drive auto-photocatalytic oxidation of benzyl alcohol and produce large quantities of $\text{H}_2\text{O}_2$ in a solvent-free (no water) or biphasic (with water) system under nominally visible light irradiation (>420 nm cutoff filter) even in the absence of any heterogeneous photocatalyst. We discuss the impact of our findings on the reliability of interpretation of photocatalytic $\text{H}_2\text{O}_2$ production in studies in which benzyl alcohol was employed as model electron donor, and provide simple check protocols for excluding similar issues when using alternative substrates.
Scheme S1. Proposed mechanism of auto-photocatalytic production of H₂O₂ from benzyl alcohol and dioxygen using benzaldehyde as a photocatalyst. Benzaldehyde is excited by light irradiation to a triplet excited state (1). The excited state of benzaldehyde abstracts hydrogen atom from benzyl alcohol under formation of a diol (2).²¹ The diol reacts with dioxygen to yield α-hydroxybenzylhydroperoxide and benzaldehyde (3). The α-hydroxybenzylhydroperoxide intermediate decomposes rapidly to H₂O₂ and benzaldehyde (4).²²,²⁹ Note that i) since benzaldehyde is the light-absorbing species and is not consumed during the reaction cycle, the conversion is truly photocatalytic; ii) since the product of benzyl alcohol oxidation is benzaldehyde, i.e. the photocatalyst, the reaction is also autocatalytic.

Experimental
Materials
Benzyl alcohol (99%, Alfa Aesar), benzaldehyde (99%, Sigma Aldrich), 1,1,2,2,-Tetrachloroethane (99 %, Sigma Aldrich), CDCl₃ (99 %, Sigma Aldrich), CD₃CN (99 %, Sigma Aldrich). Hydrogen peroxide (30 wt%, Sigma Aldrich), titanium oxysulfate sulfuric acid hydrate (TiOSO₄·xH₂O) (Synthesis grade, Sigma Aldrich). Potassium poly(heptazine imide) (KPHI) photocatalyst was prepared according to the procedure described by Lotsch et al.³⁰ Melon polymer preparation was accomplished by self-condensation of dicyandiamide in a muffle furnace at 550 °C for 4 h. The obtained yellow solid was ground, washed 4 times with deionized water by centrifugation and dried in an oven at 70 °C for 24 h. For the KPHI synthesis 1.5 g of melon polymer and 3 g of KSCN were separately dried at 140 °C for 24 h, then the powders were ground together in a mortar, put in a lid-covered ceramic crucible and heated in a muffle furnace at a rate of 30 °C min⁻¹ first to 400 °C for 1 h and then to 500 °C for 30 min. Thus, prepared KPHI samples were cooled down to room temperature and then thoroughly washed with deionized water by centrifugation for 5 times. The washed powders were dried at 70 °C for 24 h.
Photochemical benzyl alcohol conversion
Photocatalytic experiments were performed under LED UV-light irradiation (365 nm, 3.3 mW cm\(^{-2}\)), LED violet-light irradiation (406 nm, 4.2 mW cm\(^{-2}\)) or polychromatic visible light (~100 mW/cm\(^{2}\)) using an Ushio 150 W Xe lamp in a light-condensing lamp housing (LOT-Oriel GmbH) equipped with a >420 cut-off filter (Schott). If not stated otherwise, mixtures of 5 mL of water and 5 mL of benzyl alcohol containing certain amounts of benzaldehyde were vigorously stirred and irradiated. The temperature of 20 °C in the photocatalytic reactors was maintained by a water-cooling jacket. Before irradiation started, the solutions were flushed with pure O\(_2\) and sealed with rubber septa. This procedure was repeated each time after taking the samples out from the reactors for analysis. The samples of 0.1 mL (diluted if necessary, as to fit the linear range of the calibration curve) were taken at certain time intervals, mixed with 2.4 mL of H\(_2\)O and 0.5 mL of TiOSO\(_4\) solution to produce the yellow-coloured titanium peroxo complex. H\(_2\)O\(_2\) concentration was estimated by measuring the absorbance of the titanium peroxo complex solutions at 420 nm using a Cary 60 (Agilent Technologies) spectrophotometer. The calibration curve was obtained using known concentrations of H\(_2\)O\(_2\). For the identification and quantification of the organic products of the reaction, 0.3 mL of the sample from organic layer was taken after 24 h of irradiation and was mixed with 0.3 mL of CDCl\(_3\) solvent, then 25 µL of an internal standard 1,1,2,2,-tetrachloroethane was introduced. The \(^1\)H NMR spectra were measured in a Bruker Avance II 400 MHz spectrometer.

Results and discussion
In order to investigate the photochemical reactivity of biphasic systems of benzyl alcohol/benzaldehyde and water, we first irradiated a mixture composed of equal volumes of benzyl alcohol and H\(_2\)O under UV light (365 nm LED; Figure 1). Unlike the case of Pavan et al.\(^{20}\) who worked with benzyl alcohol solutions in acetonitrile, we did not observe any initiation period of benzyl alcohol photochemical conversion and H\(_2\)O\(_2\) formation in the aqueous phase (Figure 1). The irradiation of this biphasic system for 24 h yielded 2.0 mmols of H\(_2\)O\(_2\), which corresponds to the concentration of H\(_2\)O\(_2\) in the aqueous phase of 0.4 M, a very high value that is far beyond the values typically achieved in light-driven H\(_2\)O\(_2\) production\(^{16}\) The \(^1\)H NMR analysis of the organic phase confirmed the presence of benzaldehyde by the resonance at 9.9 ppm and formation of benzoic acid is also suggested by new peaks appearing in the NMR spectrum, in particular one at 8.2 ppm (Figure 1). We conclude that the reaction is most likely initiated by benzaldehyde from self-oxidation of benzyl alcohol,\(^{21, \ 22}\) and proceeds via benzaldehyde-mediated auto photocatalytic mechanism shown in Scheme 1.
In accord with the previous works on benzyl alcohol photooxidation,\textsuperscript{20,27} only small amounts of H\textsubscript{2}O\textsubscript{2} were produced by irradiation of benzyl alcohol under \textit{visible} light only (406 nm LED) (Figure 2a). The H\textsubscript{2}O\textsubscript{2} production was slightly intensified in the biphasic system containing hydrochloric acid (Figure 2a), which was likely due to a higher stability of H\textsubscript{2}O\textsubscript{2} under low pH or to its facilitated formation by reaction of the protons with reactive oxygen species. Nevertheless, such experiments in which only the substrate is irradiated to rule out any autooxidation effects in a photocatalytic system might be deceiving since they do not take into account possible photochemical activity of intermediates formed upon substrate oxidation. Hence, the same experiments were performed in the presence of 2 v/v\% of benzaldehyde which is the main product of benzyl alcohol oxidation. The formation of H\textsubscript{2}O\textsubscript{2} was observed immediately after starting the irradiation, and its concentration steadily increased throughout 24 h of irradiation, eventually yielding high amounts of H\textsubscript{2}O\textsubscript{2} (0.54 mmols) (Figure 2a). Again, the acidic pH of the aqueous phase facilitates the H\textsubscript{2}O\textsubscript{2} formation (Figure 2a), which is in agreement with what was observed by Yamashita \textit{et al.}\textsuperscript{28} Notably, the \textsuperscript{1}H NMR analysis of the organic phase after 24 h of irradiation shows that benzaldehyde was not consumed during the irradiation of the solution, but its concentration in the system even increased (Table 1, Figure 2b), confirming that it behaves as a molecular photocatalyst (Scheme 1). Surprisingly, the photoconversion of the benzyl alcohol – benzaldehyde system also took place even when using a 420 nm cut-off filter under simulated solar irradiation (~1 sun), hence nominally under \textit{visible} light (Figure 2a). Although the produced amounts of H\textsubscript{2}O\textsubscript{2} were smaller in this case than under 406 nm LED light, the concentration of H\textsubscript{2}O\textsubscript{2} reached 11 mM and 24 mM after 4 h and 24 h of irradiation, respectively. These values are comparable to those reported by Yamashita \textit{et al.}\textsuperscript{28} for the biphasic H\textsubscript{2}O\textsubscript{2} production \textit{via} benzyl alcohol oxidation under >420
nm light. Clearly, the presence of benzaldehyde in the system is responsible for photochemical production of $\text{H}_2\text{O}_2$ even under visible light irradiation. In a control experiment, the irradiation of benzaldehyde-water biphasic mixture (without benzyl alcohol) did not result in high concentrations of $\text{H}_2\text{O}_2$ in the aqueous phase, instead after short time of irradiation an insoluble precipitate, most likely benzoic acid, was formed (Table 1, Figure 2).

In order to confirm that benzyl alcohol photooxidation is initiated by benzaldehyde and not by impurities which commercial benzaldehyde might contain and to estimate the extent to which autooxidation in benzyl alcohol-benzaldehyde mixture affects the evaluation of the photocatalytic performance of semiconductor catalysts, the following experiment was carried out. Since no benchmark hydrophobic photocatalyst that could be dispersed in organic phase was available, the photocatalytic oxidation of benzyl alcohol was carried out under solvent-free monophasic conditions, i.e., in benzyl alcohol only (Figure 3), whereby a powder of potassium poly(heptazine imide) (KPHI), an ionic form of polymeric carbon nitride prepared by reported procedure, was used as a photocatalyst as it is well known to be active in photocatalytic $\text{H}_2\text{O}_2$ production. As expected, KPHI showed high activity in benzyl alcohol oxidation with concomitant $\text{H}_2\text{O}_2$ production yielding 0.61 and 0.95 mmols of $\text{H}_2\text{O}_2$ and benzaldehyde, respectively, after 24 h of irradiation (Figure 3a, Table 1). Interestingly, in another run, when after 4 h of irradiation the KPHI photocatalyst was removed from the suspension at a moment when only 0.10 mmols of $\text{H}_2\text{O}_2$ was produced, the irradiation was continued and eventually the yield of 0.50 mmols of $\text{H}_2\text{O}_2$ was obtained after 24 h (Table 1, green curve in Figure 3a). Notably, this value is rather close to that obtained when carrying out the reaction without filtering the KPHI photocatalyst off (red curve in Figure 3a). These

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**Figure 2.** Photochemical $\text{H}_2\text{O}_2$ production in benzyl alcohol (BA)-benzaldehyde (BAL) mixtures in biphasic systems. (a) $\text{H}_2\text{O}_2$ yield in the aqueous phase; (b) Selected $^1\text{H}$ NMR spectra in CDCl$_3$ with 1,1,2,2-tetrachloroethane internal standard of BA and the BAL photochemical reaction products. **Conditions:** Organic phase composed of BA-BAL mixture (5 mL), aqueous phase: H$_2$O or 0.1M HCl (5 mL), LED 406 nm (4.2 mW cm$^{-2}$), O$_2$ 1 atm, temperature 20 °C. For the orange curve the conditions are BA (4.9 mL), BAL (0.1 mL), 0.1M HCl (5 mL), vigorous stirring, O$_2$ 1 atm., 1 sun irradiation, >420 nm cut-off filter.
results clearly show that, in the system comprising the KPHI photocatalyst in benzyl alcohol, the H$_2$O$_2$ production is not only influenced but indeed dominated by the photocatalytic activity of benzaldehyde.

Notably, such H$_2$O$_2$ production photocatalyzed by benzaldehyde is not limited to systems with benzyl alcohol as electron donor. We found that ethanol is also a suitable electron and proton donor for this reaction, leading to the formation of 0.35 mmols of H$_2$O$_2$ after 24 h of irradiation under 406 nm LED (Table 1). This is in agreement with the study of Bradshaw et al.\textsuperscript{21} where it was observed that the presence of ethanol in irradiated benzaldehyde favoured formation of the geminal diol intermediate (Scheme 1, eq. 2).

The outcome of the photochemical reaction also depends on the presence of other organic solvents or water in the medium. The use of acetonitrile as solvent significantly suppressed H$_2$O$_2$ production and possibly also benzaldehyde formation (Table 1), which is in line with previous reports that found that the quenching of the excited state of benzaldehyde and the corresponding hydrogen abstraction process are conditioned by the type of the solvent.\textsuperscript{36} Moreover, a control experiment carried out by irradiating benzyl alcohol-benzaldehyde mixture under monophasic water-free and solvent-free conditions showed that even a higher amount of H$_2$O$_2$ was produced, while no increase of the benzaldehyde concentration was observed after 24 h (Table 1, black curves in Figure 3a,b).

Therefore, we now turn our attention to the fate of benzaldehyde in this photochemical system. Does benzaldehyde, once formed, undergo further transformation under irradiation and how the reaction medium affects it? A reliable identification and quantification of benzoic acid, a
possible reaction product, by $^1\text{H}$ NMR spectroscopy is complicated due to its low concentration and hydrogen bonding resulting in very broad peaks. In order to obtain more precise data regarding the formation of this compound, we reduced the reaction volume by the factor of 10 and carried out also $^{13}\text{C}$ NMR studies of the solutions after irradiation (Table 2).

Table 1. Photochemical conversion of benzyl alcohol/benzaldehyde systems under 406 nm LED irradiation

<table>
<thead>
<tr>
<th>Organic phase composition</th>
<th>Aqueous phase / solvent</th>
<th>H$_2$O$_2$ produced after 24h of irradiation (mmols)</th>
<th>Initial BAL content (mmols)</th>
<th>BAL content after 24h of irradiation (mmols)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzyl alcohol</td>
<td>Benzaldehyde</td>
<td>5 mL H$_2$O</td>
<td>0.04</td>
<td>-</td>
</tr>
<tr>
<td>5.0 mL</td>
<td>-</td>
<td>5 mL H$_2$O</td>
<td>0.09</td>
<td>-</td>
</tr>
<tr>
<td>4.9 mL</td>
<td>0.1 mL</td>
<td>5 mL H$_2$O</td>
<td>0.54</td>
<td>0.98</td>
</tr>
<tr>
<td>4.9 mL</td>
<td>0.1 mL</td>
<td>5 mL HCl 0.1M</td>
<td>0.69</td>
<td>0.98</td>
</tr>
<tr>
<td>4.9mL*</td>
<td>0.1 mL</td>
<td>5 mL HCl 0.1M</td>
<td>0.12</td>
<td>0.98</td>
</tr>
<tr>
<td>-</td>
<td>5 mL</td>
<td>5 mL H$_2$O</td>
<td>N/D</td>
<td>49.0</td>
</tr>
<tr>
<td><strong>Monophasic</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.9 mL</td>
<td>0.1 mL</td>
<td>-</td>
<td>1.15</td>
<td>0.98</td>
</tr>
<tr>
<td>5.0 mL**</td>
<td>-</td>
<td>-</td>
<td>0.61</td>
<td>-</td>
</tr>
<tr>
<td>5.0 mL***</td>
<td>-</td>
<td>-</td>
<td>0.50</td>
<td>-</td>
</tr>
<tr>
<td>2.45 mL</td>
<td>0.05 mL</td>
<td>MeCN 2.5 mL</td>
<td>0.25</td>
<td>0.49</td>
</tr>
<tr>
<td>****</td>
<td>0.5 mL</td>
<td>4.5 mL Ethanol</td>
<td>0.35</td>
<td>4.90</td>
</tr>
</tbody>
</table>

*The experiment was carried out under 1 sun solar simulated irradiation with an >420 nm cut-off filter
**In presence of KPHI photocatalyst
***In presence of KPHI photocatalyst that was filtered out after 4 h of irradiation
****The experiment was carried out with ethanol as electron and proton donor.

The irradiation of monophasic benzyl alcohol-benzaldehyde solution resulted in the decrease of initial benzyl alcohol concentration, which can be judged by the peak at 193.3 ppm (Figure 4a). Benzaldehyde content after light exposure was also reduced, which was most likely due to its further oxidation to benzoic acid (BAc), as confirmed by appearance of a peak at 170.2 ppm (Table 2, Figure 4a). On the other hand, the photooxidation in the biphasic benzyl alcohol-benzaldehyde/water mixture does not lead to benzaldehyde overoxidation to benzoic acid and an increase of benzaldehyde concentration with respect to the initial one can be observed (Table 2, Figure 4a). The same reaction using an organic solvent (acetonitrile) did
not lead to the formation of detectable amounts of H₂O₂ and resulted only in slight conversion of benzyl alcohol, significantly lower than that observed in solvent-free conditions (Table 2). The photooxidation of pure benzaldehyde immediately yields an insoluble precipitate in the vial, which, according to 13C NMR analysis, is benzoic acid. Almost quantitative conversion of benzaldehyde to benzoic acid can be observed after 24 h of irradiation similar to the case reported by Mazzanti et al.37 (Figure 4b, Table 2).

Table 2. Quantification of benzyl alcohol-benzaldehyde photochemical reaction products under 406 nm irradiation

<table>
<thead>
<tr>
<th>Organic phase composition</th>
<th>Aqueous phase/solvent</th>
<th>H₂O₂ produced after 24h of irradiation (mmols)</th>
<th>BA content after 24h of irradiation (mmols)</th>
<th>BAL content after 24h of irradiation (mmols)</th>
<th>BAc content after 24h of irradiation (mmols)**</th>
</tr>
</thead>
<tbody>
<tr>
<td>BA</td>
<td>BAL</td>
<td>-</td>
<td>0.116</td>
<td>2.80</td>
<td>0.54</td>
</tr>
<tr>
<td>0.4 mL/3.85 mmols</td>
<td>0.1 mL/0.98 mmols*</td>
<td>0.5 mL H₂O</td>
<td>0.137</td>
<td>3.71</td>
<td>0.96</td>
</tr>
<tr>
<td>0.4 mL/4.0 mmols**</td>
<td>0.1 mL/0.87 mmols**</td>
<td>0.3 mL CD₃CN</td>
<td>-</td>
<td>2.32</td>
<td>0.53</td>
</tr>
<tr>
<td>0.24 mL/2.48 mmols**</td>
<td>0.06 mL/0.46 mmols**</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.07</td>
</tr>
</tbody>
</table>

Conditions: Organic phase composed of BA-BAL mixture (0.5 mL), LED 406 nm (40 mW cm⁻²), O₂ 1 atm., temperature 20 °C.

*Calculated values

**The values determined from ¹H NMR spectra of the solutions

***The values determined from ¹³C NMR spectra of the solutions
The presented data unambiguously show that benzaldehyde-mediated photooxidation of benzyl alcohol and concomitant H₂O₂ production must be accounted for in studies of light-driven H₂O₂ production using heterogeneous photocatalysis and benzyl alcohol as electron donor, even under nominally visible light (using a 420 nm cut-off filter).¹⁷, ¹⁸ The observed effects might be negligible in very dilute solutions of benzyl alcohol, but they might represent a dominant mechanism under solvent-free (only benzyl alcohol) or biphasic (e.g., equimolar benzyl alcohol/water mixtures) conditions.³⁸⁻⁴³ Two further points are noteworthy with respect to the visible light activity. Firstly, the designation of a 420 nm cut-off filter implies, per definitionem, that the transmittance at 420 nm is 50%, i.e., there can be a small portion of higher energy light still transmitted when using these filters. Therefore, it makes sense, as we do, to speak about experiments carried out under nominally visible light irradiation when using a 420 nm cut-off filter. Secondly, pure benzaldehyde does absorb significant portion of visible light, and its absorption tail extends down to 420-430 nm range (Figure 5). Moreover, the absorption edge of benzaldehyde apparently depends on the choice of solvent. As an example, one can see a red shift of benzaldehyde absorption edge if it is dissolved in ethanol compared to that dissolved in acetonitrile (Figure 5). The solvent-benzaldehyde interaction can affect the clustering of benzaldehyde molecules, disrupting the π-π interactions in the system and hence influencing the electronic excitation of benzaldehyde. It is likely that especially under solvent-free and biphasic conditions, the π-π interactions are beneficial for photoexcitation of benzaldehyde at longer wavelengths, leading to the formation of excited states that can react with benzyl alcohol, and resulting in simultaneous benzaldehyde and H₂O₂ formation according to the mechanism depicted in Scheme 1.
Figure 5. Optical absorption of benzyl alcohol and benzaldehyde. (a) UV-vis electronic absorption spectra without solvents and dissolved in MeCN or ethanol and (b) the magnified 390–430 nm range of the same spectra.

Conclusions

To summarize, we demonstrated the ability of benzaldehyde to promote photochemical oxidation of benzyl alcohol and produce large quantities of H$_2$O$_2$ in a solvent-free (no water) or biphasic (with water) system even under nominally visible light (using a >420 nm cutoff filter) irradiation. Interestingly, for example, in a biphasic system of benzyl alcohol and water and using only benzaldehyde as a photocatalyst, H$_2$O$_2$ concentrations exceeding those reported for most semiconductor-mediated light-driven H$_2$O production systems can be achieved. Interestingly, as we found that benzaldehyde-mediated photocatalysis of H$_2$O$_2$ productions proceeds also using alternative electron donors such as ethanol, these results definitely pave the way for a more general use of benzaldehyde in visible light-driven photocatalysis. On the other hand, our findings also shed some critical light on a number of research reports on photocatalytic H$_2$O$_2$ production in which benzyl alcohol has been employed as electron donor. Since the auto-photocatalytic pathway initiated by the light absorption by benzaldehyde formed during photocatalysis under such conditions cannot be neglected in many cases, the interpretations of photocatalytic performance of various photocatalysts are likely contentious and distorted in such reports. Therefore, we conclude that the use of benzyl alcohol as a model electron donor in photocatalytic studies should be definitely discouraged. More generally, similar effects cannot be a priori ruled out also in case of other substrates and other photocatalytic reactions. In order to exclude the possibility that a heterogeneous photocatalytic reaction is significantly influenced by photoactivity of a reaction intermediate, a simple check protocol is mandatory that consists in filtering off the heterogeneous photocatalyst in the course of reaction and checking how much the rate of the reaction is changed by the absence of the heterogeneous photocatalyst.
Acknowledgements

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