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Benzaldehyde-Promoted (Auto)Photocatalysis under Visible Light: Pitfalls and Opportunities in Photocatalytic H₂O₂ Production**

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This article is dedicated to Professor Horst Kisch on the occasion of his 80th birthday.

Selective photooxidation of aromatic alcohols to corresponding aldehydes is a widely used model reaction for evaluation of performance of heterogeneous photocatalysts. A top example is the photocatalytic production of hydrogen peroxide *via* reduction of dioxygen with concomitant photooxidation of benzyl alcohol to benzaldehyde. Herein we demonstrate the ability of benzaldehyde to promote the auto-photocatalytic oxidation of benzyl alcohol and produce large quantities of H₂O₂ in solvent-free (no water) or biphasic (with water) systems even under nominally visible (>420 nm cut-off filter) light irradiation. These results shed critical light on the plethora of research reports on photocatalytic H₂O₂ 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. The use of benzyl alcohol as a model electron donor in photocatalytic studies should be therefore definitely discouraged. On the other hand, as we found that benzaldehyde-mediated photocatalysis of H₂O₂ production proceeds also using alternative electron donors (*e.g.*, ethanol), our results highlight the possible prospects for a more general use of benzaldehyde and other aromatic aldehydes in visible light-driven photocatalysis.

Introduction

Heterogeneous photocatalysis represents a vibrant research field^[1] with possible applications ranging from water detoxification^[2] to solar fuel generation^[3] and chemical synthesis.^[4] 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.^[5] 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.^[6] As a rule, a blank test intended to confirm the photocatalytic nature of the reaction is typically 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 consider the photochemical behavior of products of partial oxidation of aromatic alcohols formed during irradiation of the suspension of photocatalysts in the substrate solution.

Herein, we demonstrate that benzaldehyde, the product of benzyl alcohol oxidation, can itself act as a highly efficient, visible light-active photocatalyst for H₂O₂ production *via* reduction of oxygen and oxidation of alcohols. That the photocatalytic role of benzaldehyde in light-driven systems for H₂O₂ production has not been hitherto recognized is particularly puzzling given the fact that the photochemical properties of various aldehydes, including formation of reactive radicals upon photoexcitation, have been long known; see a recent review by Kokotos *et al.*^[7] It is also established that the benzaldehyde triplet excited state can be effectively quenched by triplet-state energy acceptors,^[8] and, when dissolved in a good hydrogen donor, it can perform hydrogen abstraction leading to the formation α -hydroxybenzyl radical in general,^[9] or of diols in the presence of alcohols.^[10] In 2016, the Augugliaro group reported the photocatalytic effect of *ortho*-methoxybenzaldehyde, produced by oxidation of *ortho*-methoxybenzyl alcohol over TiO₂ photocatalysts, on homogeneous photooxidation of other alcohols under UV light.^[11] Surprisingly, this important finding that should have alarmed many

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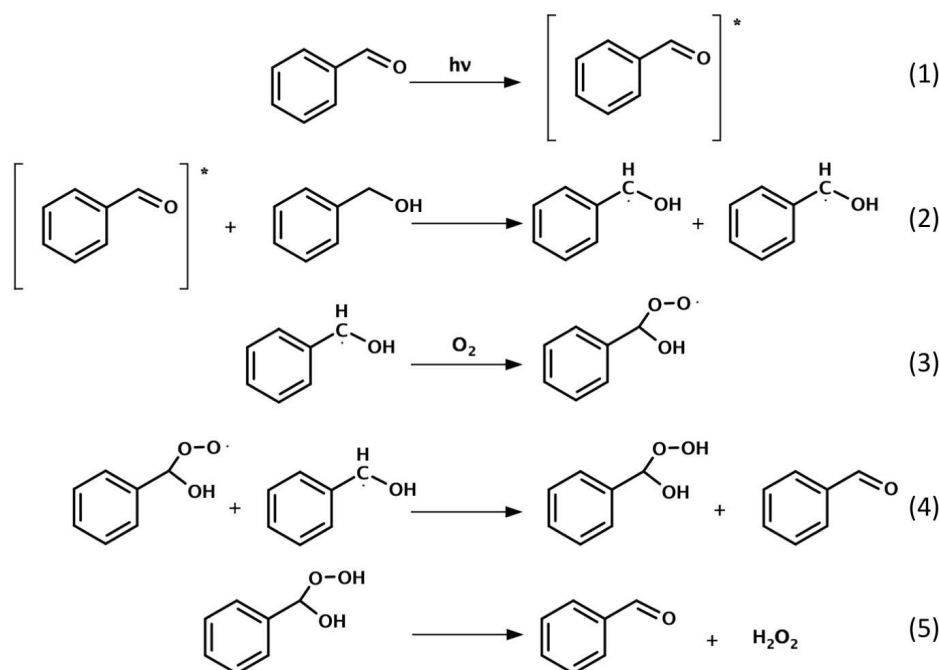
[**] A previous version of this manuscript has been deposited on a preprint server (<https://doi.org/10.26434/chemrxiv-2022-sg5mt>).

Supporting information for this article is available on the WWW under <https://doi.org/10.1002/cctc.202201215>

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researchers has been sadly neglected by the community, as this paper has received only few citations so far. Two years later, Pavan *et al.* addressed the question of benzyl alcohol self-oxidation under UV-light.^[12] 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 TiO₂ photocatalyst showed that benzaldehyde was produced immediately upon starting irradiation; however, when the TiO₂ 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, we assume that the formed benzaldehyde initiated a photochemical reaction with benzyl alcohol leading to the oxidation of the latter to benzaldehyde according to the mechanistic steps adapted from Bradshaw,^[10a] Heyes^[13] and Pavan^[12] and shown in Scheme 1, yielding eventually, in the presence of oxygen, H₂O₂ as a byproduct. Arcas *et al.* attempted to provide 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 H₂O₂ under UV light.^[14] However, it was not clear which species was responsible for the formation of singlet oxygen. Notably, the studies of Pavan *et al.*^[12] and Arcas *et al.*^[14] concluded that the so-called autooxidation of benzyl alcohol occurs only under UV-light and that it is completely inhibited already at 405 nm.^[12]

An illustrative example that alerted our suspicion that the peculiar photochemistry of benzaldehyde might have a significant, yet unrecognized, effect on estimation of photocatalytic H₂O₂ production when using benzyl alcohol as electron donor can be found in a recent paper by Yamashita *et al.*^[15] The authors reported enhanced photocatalytic H₂O₂ 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 H₂O₂ 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 H₂O₂. Nevertheless, the profiles of the H₂O₂ evolution reported by Yamashita *et al.*^[15] clearly suggest that an autocatalytic mechanism might be at play since the H₂O₂ production was accelerated after certain irradiation time.^[15] This prompted us to investigate the issue of benzaldehyde-mediated auto-photocatalysis in H₂O₂ 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 H₂O₂ 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 H₂O₂ production in studies in which benzyl



Scheme 1. 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 producing two α -hydroxybenzyl radicals (2).^[13] One α -hydroxybenzyl radical reacts with dioxygen to yield α -hydroxybenzylperoxy radical (3). The α -hydroxybenzylperoxy and α -hydroxybenzyl radicals react with each other yielding α -hydroxybenzyl hydroperoxide and benzaldehyde (4). The α -hydroxybenzyl hydroperoxide intermediate decomposes rapidly to H₂O₂ and another benzaldehyde molecule (5).^[13,16] 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*.

alcohol was employed as model electron donor, provide simple check protocols for excluding similar issues when using alternative substrates, and highlight the interesting prospects of employing various aromatic aldehydes as photocatalysts for visible light-driven H_2O_2 production.

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_2O under UV light (365 nm LED; Figure 1). Unlike the case of Pavan *et al.*^[12] who worked with benzyl alcohol solutions in acetonitrile, we did not observe any initiation period of benzyl alcohol photochemical conversion and H_2O_2 formation in the aqueous phase (Figure 1). The UV irradiation of

this biphasic system for 24 h yielded 2.0 mmols of H_2O_2 , which corresponds to the concentration of H_2O_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_2O_2 production!^[6a] The ^1H 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,^[10a,13] and proceeds *via* benzaldehyde-mediated auto-photocatalytic mechanism shown in Scheme 1.

In accord with the previous works on benzyl alcohol photooxidation,^[12,14] only small amounts of H_2O_2 were produced by irradiation of benzyl alcohol under *visible* light only (406 nm LED) (Figure 2a). The H_2O_2 production was slightly intensified in the biphasic system containing hydrochloric acid (Figure 2a),

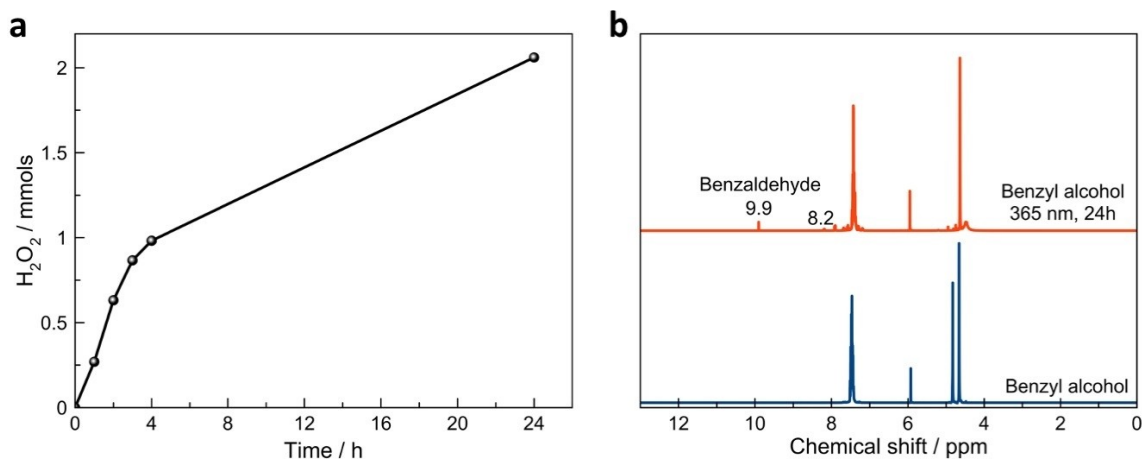


Figure 1. Photochemical H_2O_2 production *via* photooxidation of benzyl alcohol (BA) in a biphasic (BA/water) system under UV light. (a) H_2O_2 yield in the aqueous phase; (b) ^1H NMR spectra in CDCl_3 with 1,1,2,2-tetrachloroethane internal standard of BA and the BAL photochemical reaction products. *Conditions:* Benzyl alcohol (5 mL), H_2O (5 mL), LED 365 nm (3.3 mW cm^{-2}), vigorous stirring, O_2 1 atm, temperature 20°C .

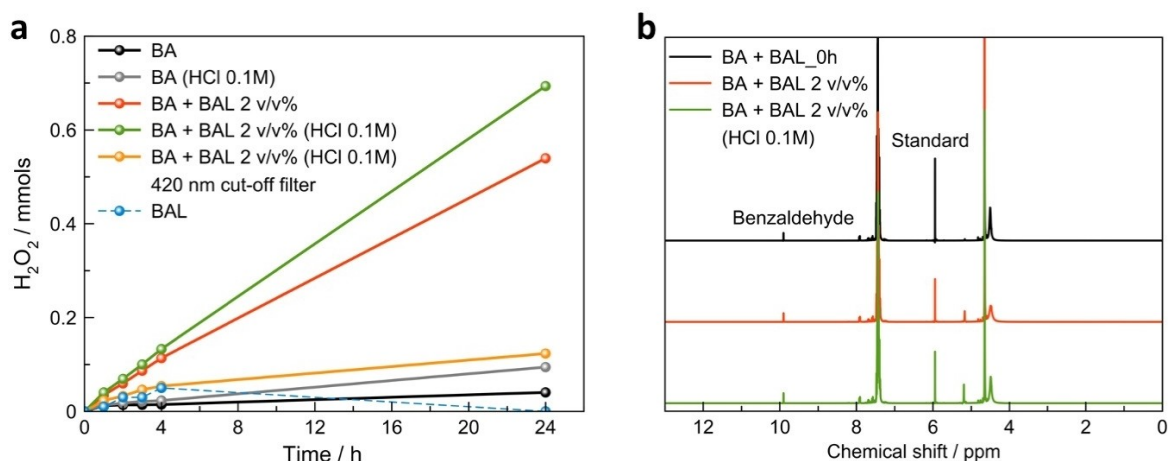


Figure 2. Photochemical H_2O_2 production in benzyl alcohol (BA)-benzaldehyde (BAL) mixtures in biphasic systems. (a) H_2O_2 yield in the aqueous phase; (b) Selected ^1H NMR spectra in CDCl_3 with 1,1,2,2-tetrachloroethane internal standard of BA and the BAL photochemical reaction products. *Conditions:* Organic phase composed of BA-BAL mixture (5 mL), aqueous phase: H_2O or 0.1 M 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), 0.1 M HCl (5 mL), vigorous stirring, O_2 1 atm, 1 sun irradiation, $>420 \text{ nm}$ cut-off filter.

which was likely due to a higher stability of H₂O₂ under low pH or due 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 consider 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 H₂O₂ was observed immediately after starting the irradiation, and its concentration steadily increased throughout 24 h of irradiation, eventually yielding high amounts of H₂O₂ (0.54 mmols) (Figure 2a). Again, the acidic pH of the aqueous phase facilitates the H₂O₂ formation (Figure 2a), which is in agreement with what was observed by Yamashita *et al.*^[15] Notably, the ¹H 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 *visible* light (Figure 2a). Although the produced amounts of H₂O₂ were smaller in this case than under 406 nm LED light, the concentration of H₂O₂ reached 11 mM and 24 mM after 4 h and 24 h of irradiation, respectively. These values are comparable to those reported by Yamashita *et al.*^[15] for the biphasic H₂O₂ production *via* benzyl alcohol oxidation under >420 nm light. Clearly, the presence of benzaldehyde in the system is responsible for photochemical production of H₂O₂ 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 H₂O₂ in the aqueous phase, instead after short time of irradiation an insoluble precipitate,

most likely benzoic acid, was formed (Table 1, Figure 2). In another control experiment, where a 450 nm LED source was used for irradiation, the activity of benzaldehyde as photocatalyst for H₂O₂ was found almost negligible (Table 1). This clearly corroborates the photochemical rather than the thermal autocatalytic nature of H₂O₂ generation.

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^[17] prepared by reported procedure,^[18] was used as a photocatalyst, as it is well known to be active in photocatalytic H₂O₂ production.^[4b,19] As expected, KPHI showed high activity in benzyl alcohol oxidation with concomitant H₂O₂ production yielding 0.61 and 0.95 mmols of H₂O₂ 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 H₂O₂ was produced, the irradiation was continued and eventually the yield of 0.50 mmols of H₂O₂ 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 results clearly show that, in the system comprising the KPHI photocatalyst in benzyl alcohol, the H₂O₂ production is not only influenced but indeed dominated by the photocatalytic activity of benzaldehyde.

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

Organic phase composition		Aqueous phase/solvent	H ₂ O ₂ produced after 24 h of irradiation [mmols]	Initial BAL content [mmols]	BAL content after 24 h of irradiation [mmols]
Benzyl alcohol	Benzaldehyde				
5.0 mL	–	5 mL H ₂ O	0.04	–	–
5.0 mL	–	5 mL HCl 0.1 M	0.09	–	–
4.9 mL	0.1 mL	5 mL H ₂ O	0.54	0.98	1.94
4.9 mL	0.1 mL	5 mL HCl 0.1 M	0.69	0.98	2.02
4.9 mL ^[a]	0.1 mL	5 mL HCl 0.1 M	0.12	0.98	–
4.9 mL ^[b]	0.1 mL	5 mL H ₂ O	0.024±0.004	0.98	–
–	5 mL	5 mL H ₂ O	N/D	49.0	–
Monophasic					
4.9 mL	0.1 mL	–	1.15	0.98	0.93
5.0 mL ^[c]	–	–	0.61	–	0.95
5.0 mL ^[d]	–	–	0.50	–	0.16
2.45 mL	0.05 mL	MeCN	0.25	0.49	0.40
–	–	2.5 mL	–	–	–
– ^[e]	0.5 mL	4.5 mL Ethanol	0.35	4.90	Not determined

[a] The experiment was carried out under 1 sun solar simulated irradiation with a >420 nm cut-off filter, [b] The experiment was carried out under 450 nm LED irradiation (4.2 mW cm⁻²), [c] In presence of KPHI photocatalyst, [d] In presence of KPHI photocatalyst that was filtered out after 4 h of irradiation, [e] The experiment was carried out with ethanol as electron and proton donor.

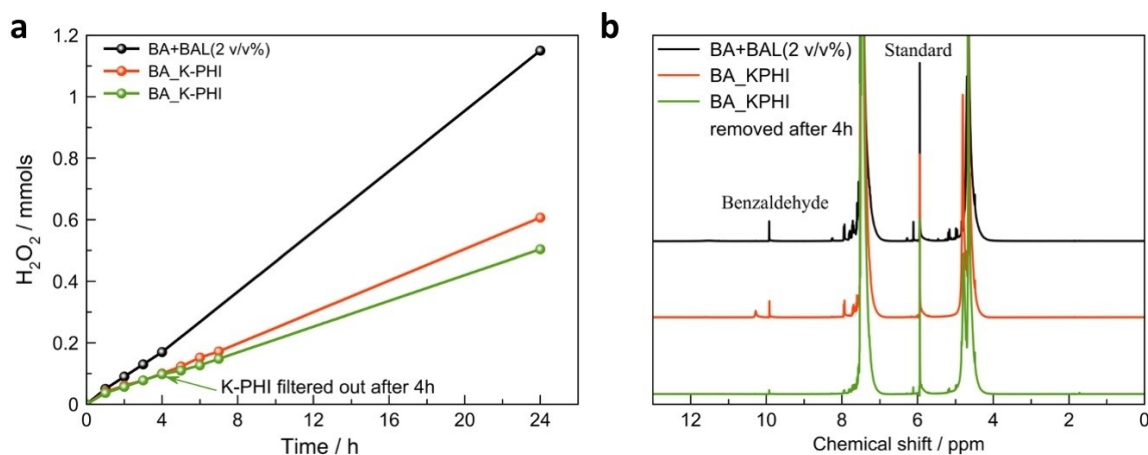


Figure 3. Photocatalytic H_2O_2 production under visible light by solvent-free monophasic (*i.e.*, in benzyl alcohol only) conversion of benzyl alcohol in the presence or absence of a KPHI photocatalyst. (a) H_2O_2 yield; for the green curve, KPHI photocatalysts was filtered out of the suspension by a $0.25\ \mu\text{m}$ filter after 4 h of irradiation. (b) Selected ^1H NMR spectra in CDCl_3 with 1,1,2,2-tetrachloroethane internal standard of the photochemical reaction products. Conditions: BA (5 mL), K-PHI 5 mg, LED 406 nm ($4.2\ \text{mWcm}^{-2}$), vigorous stirring, O_2 1 atm, temperature 20°C .

Notably, such H_2O_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_2O_2 after 24 h of irradiation under 406 nm LED (Table 1). 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_2O_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.^[20] Moreover, a control experiment carried out by irradiating benzyl alcohol-benzaldehyde mixture under monophasic (water-free) conditions showed that even a higher amount of H_2O_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 ^1H 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}C NMR studies of the solutions after irradiation (Table 2).

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 photo-oxidation 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

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

Organic phase composition		Aqueous phase/solvent	H_2O_2 produced after 24 h of irradiation [mmols]	BA content after 24 h of irradiation [mmols]	BAL content after 24 h of irradiation [mmols]	BAC content after 24 h of irradiation [mmols] ^[c]
BA	BAL					
0.4 mL/ 3.85 mmols	0.1 mL/ 0.98 mmols ^[a]	–	0.116	2.80	0.54	0.30
0.4 mL/ 4.0 mmols ^[b]	0.1 mL/ 0.87 mmols ^[b]	0.5 mL H_2O	0.137	3.71	0.96	–
0.24 mL/ 2.48 mmols ^[b]	0.06 mL/ 0.46 mmols ^[b]	0.3 mL CD_3CN	–	2.32	0.53	–
–	0.1 mL/ 0.98 mmols ^[a]	–	–	–	0.07	0.78

Conditions: Organic phase composed of BA-BAL mixture (0.5 mL), LED 406 nm ($40\ \text{mWcm}^{-2}$), O_2 1 atm, temperature 20°C .

[a] Calculated values, [b] The values determined from ^1H NMR spectra of the solutions, [c] The values determined from ^{13}C NMR spectra of the solutions

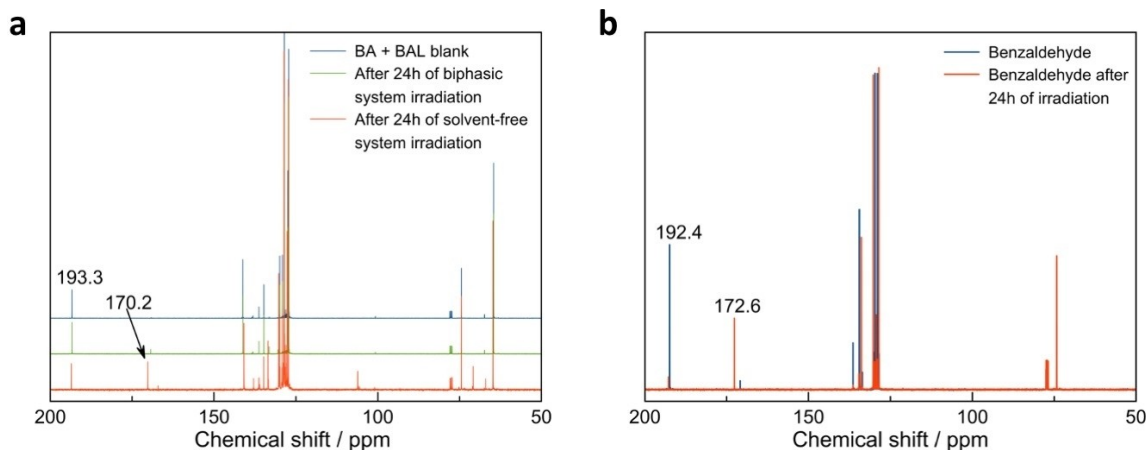


Figure 4. NMR analysis of reaction products. (a) The comparison of ¹³C NMR spectra in CDCl₃ with 1,1,2,2-tetrachloroethane internal standard of BA and the BAL photochemical reaction products formed in presence and absence of aqueous phase. Conditions for the blue and red lines: Benzyl alcohol (0.4 mL), benzaldehyde (0.1 mL), LED 406 nm (40 mW cm⁻²), vigorous stirring, O₂ 1 atm. Conditions for the green line: Benzyl alcohol (0.4 mL), benzaldehyde (0.1 mL), H₂O (0.5 mL), LED 406 nm (40 mW cm⁻²), vigorous stirring, O₂ 1 atm. (b) ¹³C NMR spectra in CDCl₃ with 1,1,2,2-tetrachloroethane internal standard of the BAL photochemical reaction products. Conditions: Benzaldehyde (0.1 mL), LED 406 nm (40 mW cm⁻²), O₂ 1 atm.

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.*^[21] (Figure 4b, Table 2).

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).^[6b,c] 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.*, equi-volumetric benzyl alcohol/water mixtures) conditions.^[22] 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). The absence of the light absorption by benzaldehyde at longer wavelengths explains the almost complete inhibition of the photochemical production of H₂O₂ if the system is irradiated using a 450 nm LED (Table 1). Moreover, the absorption edge of benzaldehyde

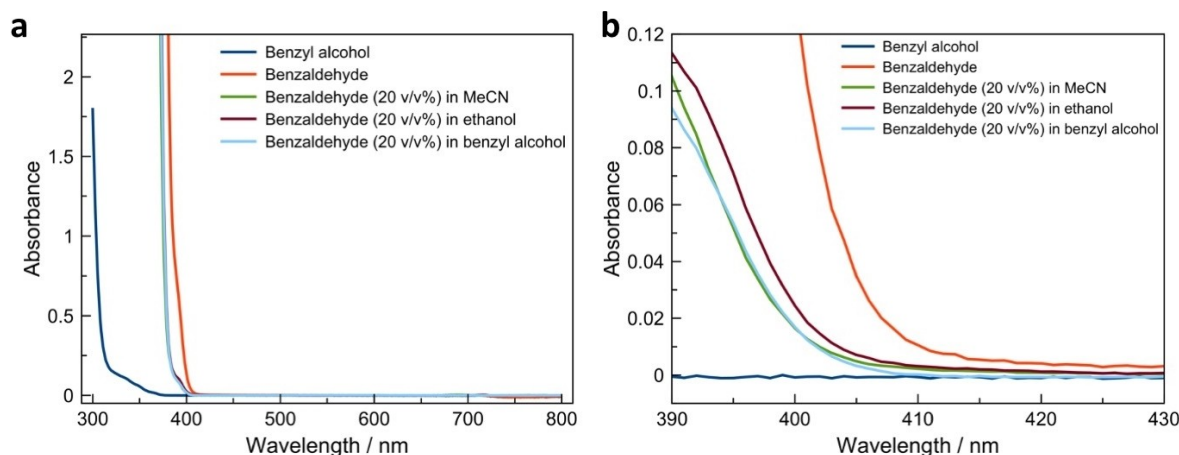


Figure 5. Optical absorption of benzyl alcohol and benzaldehyde. (a) UV-vis electronic absorption spectra without solvents and dissolved in MeCN or ethanol and (b) the magnified 390–430 nm range of the same spectra.

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 or benzyl alcohol (Figure 5). The solvent-benzaldehyde interaction can affect the light absorption of benzaldehyde. One can clearly see the bathochromic shift caused by H-bonding solvent like ethanol as compared to MeCN (Figure 5). Benzyl alcohol, although also possessing a hydroxyl group has lower polarity than ethanol and does not induce a similar bathochromic shift of the benzaldehyde light absorption.

Conclusions

To summarize, we demonstrated the ability of benzaldehyde to promote photochemical oxidation of benzyl alcohol and produce large quantities of H_2O_2 in solvent-free (no water) or biphasic (with water) systems 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_2O_2 concentrations exceeding those reported for most semiconductor-mediated light-driven H_2O production systems can be achieved. These findings therefore shed some critical light on a number of research reports on photocatalytic H_2O_2 production in which benzyl alcohol has been employed as electron donor.^[6b,22a-c] 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. More positively, as we found that benzaldehyde-mediated photocatalysis of H_2O_2 production proceeds also using alternative electron donors such as ethanol, our results highlight the prospects for a more general use of benzaldehyde and other aromatic aldehydes in visible light-driven photocatalysis.^[6b] Experimental work along this line is currently underway in our laboratory.

Experimental

Materials

Benzyl alcohol (99%, Alfa Aesar), benzaldehyde (99%, Sigma Aldrich), 1,1,2,2-Tetrachloroethane (99%, Sigma Aldrich), CDCl_3 (99%, Sigma Aldrich), CD_3CN (99%, Sigma Aldrich). Hydrogen peroxide (30 wt%, Sigma Aldrich), titanium oxysulfate sulfuric acid

hydrate ($\text{TiOSO}_4 \cdot x\text{H}_2\text{O}$) (Synthesis grade, Sigma Aldrich). Potassium poly(heptazine imide) (KPHI) photocatalyst was prepared according to the procedure described by Lotsch *et al.*^[18] 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 $30^\circ\text{C min}^{-1}$ 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}), Nichia NVSU233A-D1 LED violet-light irradiation (406 nm, 4.2 mW cm^{-2}) with the FWHM of 16 nm. The optical spectrum of the LED 406 nm was measured by using an MSC15 spectral light meter (Gigahertz-Optic GmbH) (see Supporting Information, Figure S1). The source of polychromatic visible light (~ 100 mW/cm^2) was an Ushio 150 W Xe lamp in a light-condensing lamp housing (LOT-Oriel GmbH) equipped with a >420 cut-off filter (Schott) (for the transmittance of the cut-off filter see Supporting Information, Figure S2). 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_2O and 0.5 mL of TiOSO_4 solution to produce the yellow-colored titanium peroxy complex. In case of water-free systems, the produced H_2O_2 was extracted from benzyl alcohol phase into the added aqueous phase prior to analysis. H_2O_2 concentration was estimated by measuring the absorbance of the titanium peroxy complex solutions at 420 nm using a Cary 60 (Agilent Technologies) spectrophotometer. The calibration curve was obtained using known concentrations of H_2O_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 ^1H NMR spectra were measured in a Bruker Avance II 400 MHz spectrometer.

Acknowledgements

This work was funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – Projektnummer BE 5102/5-1 and 364549901 – TRR 234 CataLight [Project B6]. IK acknowledges support by Spanish MCINN (PID2020-113558RB-C41) and Gobierno del Principado de Asturias (IDI-2021-000048) and the Alexander von Humboldt Foundation through the Humboldt Research Fellowship. Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are openly available in Zenodo at 10.5281/zenodo.7447750, reference number 7447750.

Keywords: autocatalysis · benzyl alcohol · benzaldehyde · hydrogen peroxide, photocatalysis · visible light

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Manuscript received: October 7, 2022
Revised manuscript received: December 16, 2022
Accepted manuscript online: December 19, 2022
Version of record online: January 13, 2023