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# Photo-tunable oxidation of toluene and its derivatives catalyzed by TBATB



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# ABSTRACT

In this report, tetrabutylammonium tribromide (TBATB) was introduced as an efficient visible light active catalyst to carry out the aerobic oxidation of toluene, its derivatives, and some of methyl arenes to benzaldehydes, benzoic acids and ketones in good to high yields. All the oxidation reactions were performed under mild conditions using oxygen as a green oxidant, a catalytic amount of TBATB under blue (460 nm), royal blue (430 nm), and violet LED (400 nm) irradiation. It was found that the reactions selectivity was significantly affected by changing the solvent (from CH<sub>3</sub>CN to EtOAc) and LED wavelength (from blue to violet). In the following, our mechanistic studies revealed that the visible light oxidation of toluenes and methyl arenes over TBATB could be following a benzyl peroxy radical intermediate.

# 1. Introduction

Tunable synthesis is a powerful and valuable approach to direct a reaction to a particular product. Tunable synthesis of benzaldehydes and benzoic acids via oxidation of toluene and its derivatives has great importance in organic chemistry. In recent years, valuable studies have been conducted relating to the oxidation of toluene to the more useful products like benzaldehyde and benzoic acid as essential materials for organic synthesis, antibacterial, biological and pharmaceutical applications [1–8].

Molecular oxygen as a green oxidant has been widely used in the oxidation of toluene and its derivatives [9-13]. Photocatalytic reactions have been considered from both technological and economical viewpoints due to providing a clean, short, and direct route [14,15]. Among different aerobic oxidation processes, photocatalytic oxidation has gained popularity. Recently, several studies relating to the aerobic photooxidation of toluene have been reported [1,9,16-20]. Bi<sub>2</sub>MoO<sub>6</sub> nanosheets with different thicknesses were prepared and examined in the photooxidation of toluene to benzaldehyde under irradiation of Xenon lamp (300 W): Low toluene conversion and high selectivity to benzaldehyde were obtained in the best case [1]. Pd/Bi<sub>2</sub>WO<sub>6</sub> was used for the selective aerobic photooxidation of toluene and its derivatives under visible light irradiation ( $\lambda > 400$  nm): Low toluene conversion and high benzaldehyde selectivity was obtained in the best reaction condition [9]. H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>-TiO<sub>2</sub> composites utilized for the selective photooxidation of toluene led to low toluene conversion and high selectivity to benzaldehyde [16]. Photooxidation of toluene over  $\text{TiO}_2$ -pillared montmorillonite under UV light irradiation led to the production of benzaldehyde and para-cresol as main intermediates [19]. Photooxidation of low amount of toluene in the presence of 2-chloroanthraquinone as an organophotocatalyst led to the production of high conversion of toluene to benzoic acid under irradiation of fluorescent lamp (400 nm  $<\lambda < 450$  nm) [20].

On the other hand, photocatalysts of bromo sources such as lithium bromide [21,22], bromine, hydrobromic acid [23], N-bromosuccinimide [24], MgBr<sub>2</sub>-Et<sub>2</sub>O [25], AlBr<sub>3</sub>.6H<sub>2</sub>O [26], CBr<sub>4</sub> [27], and allyl bromide [28] have shown a high potential for aerobic photooxidation reactions; the photocatalytic oxidation of toluene and its derivatives over LiBr under UV irradiation was reported by the Itoh group; benzoic acids were obtained in good to high yield in the best case [22]. The aerobic photooxidation of a low amount of toluene over a catalytic amount of allyl bromide under xenon lamp irradiation was reported by Sugai and Itoh; benzoic acids were obtained in good to high yield in the best condition [28]. Also, the photooxidation of low amount of toluene and its derivatives over CBr<sub>4</sub> and triphenylphosphine under fluorescent lamps irradiation was reported by Sugai and Itoh; benzoic acids were obtained in good to high yield in the best reaction condition [29]. The selective photooxidation of methylarenes (1 mmol) to aldehydes over (0.1 mmol) CBr<sub>4</sub> in CH<sub>3</sub>CN under irradiation of 18 W CFL (380-740 nm) was reported by Tripathi, et al. [27], however, we reported photo-tunable oxidation of toluenes (1 mmol) to benzoic acids or benzaldehydes over lower amount of TBATB as a bromo source

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photocatalyst (0.02-0.04 mmol) in EtOAc and CH<sub>3</sub>CN under irradiation of violet, royal blue, and blue LED (400, 430, and 460 nm). Some of the strategies in the selective aerobic photooxidation of toluene have been shown in Scheme 1.

Tetrabutylammonium tribromide (TBATB) is a safe, stable, and mild solid source of bromine which has been used as a brominating agent in several chemical reactions [30–37]. Recently, several research groups have tried to cleavage the silyl ethers and oxidize alcohols with a stoichiometric amount of TBATB [38–40], while for the first time we used a catalytic amount of TBATB as an excellent photocatalyst in metal free photopolymerization of vinyl monomers [41], selective photooxidation of benzyl alcohols, and oxidative-desilylation of silyl ethers [42]: 1 mmol of benzyl alcohols or tert-butyldimethylsilyl ethers converted successfully to the benzaldehyde in high yield (98 %) over 10–20 mg TBATB under air atmosphere and blue LED irradiation (460 nm) in CH<sub>3</sub>CN. Also, by changing the LED wavelength from 460 to 400 nm, benzyl alcohols transformed into the benzoic acids in high yields [42]. In fact, by changing the LED wavelength, benzaldehyde-benzoic acid synthesis could be tuned.

Because of the valuable results which were achieved in photooxidation of benzyl alcohols and the probable radical mechanism which can be operated in the photooxidation of toluene, we decided to investigate aerobic photooxidation of toluene over a catalytic amount of TBATB. Here, we have reported a tunable aerobic photooxidation of toluene and its derivatives to the corresponding benzaldehydes and benzoic acids in good to high yield over TBATB at room temperature under O<sub>2</sub> and LED irradiation. Unlike the other studies in which a low amount of toluene (0.3 mmol) has been oxidized [20,28,29] or UV lamps was as light sources [19,22], in this study we oxidized higher amount of toluene (1-2 mmol) to the corresponding oxidation products under mild reaction condition and LED light sources.



**Scheme 1.** Some of the strategies in the aerobic photooxidation of toluene to benzaldehyde and benzoic acid under light irradiation.

#### 2. Experimental

#### 2.1. Materials

Tetrabutylammonium tribromide (TBATB) (>98 %) was purchased from Acros (Acros, 123970250). Ethylbenzene ( $\geq$ 99.5 %), p-nitrotoluene (99 %), o-nitrotoluene ( $\geq$ 99 %), p-methoxytoluene (99 %), p-chlorotoluene (98 %), cumene (98 %), fluorene (98 %), o-xylene ( $\geq$ 99 %), p-toluidine (99.6 %), diphenylmethane (99 %), adamantane ( $\geq$ 99 %), and diphenylacetic acid (99 %) were provided from Merck Company. p-Bromotoluene (98 %), 1-bromo-4-ethylbenzene (97 %), and p-iodotoluene (99 %) were purchased from Sigma-Aldrich Company. p-Cresol ( $\geq$ 99 %), and p-toluic acid (98 %) were purchased from Fluka Company. Ethyl acetate and acetonitrile (Laboratory grade) were purchased from Dr-Mojalali Company (Iran). All of the chemicals and solvents used without further purification.

# 2.2. Instruments

The gas chromatography (GC) method was utilized for the detection of products. GC chromatograms were recorded using a VARIAN CP-3800 Gas Chromatograph instrument. <sup>13</sup>C NMR and <sup>1</sup>H NMR spectra of synthesized products were recorded with a Bruker 400 MHz AVANCE III spectrometer. The light sources utilized in the photooxidation reactions were violet (400 nm), royal blue (430 nm), and blue (460 nm) LED Epistar 3 W 20–30LM 700 mA h light bulbs.

# 2.3. General experimental procedure for the Photocatalytic Oxidation of toluene

0.02-0.04 mmol of TBATB and 1 mmol of toluene were added to 10 mL solvent (CH<sub>3</sub>CN or EtOAc) in a round-bottomed flask (Pyrex). Afterward, the reaction mixture was exposed to LED lamps irradiation (3 blue or 5 violet LED lamps) under an oxygen atmosphere (O<sub>2</sub>-balloon) and stirring at room temperature (Fig. S1). The resulted products were isolated by silica gel-coated TLC plates in EtOAc and n-hexane (1:9) solvent.

# 3. Results and discussion

In order to find the best reaction condition for photooxidation of 1 mmol toluene to benzaldehyde or benzoic acid over TBATB (photocatalyst), reactions were performed in the presence of various amount of TBATB, different solvents, and under irradiation of violet (400 nm) and blue (460 nm) LED at room temperature. The effect of reaction parameters such as TBATB, solvent, LED wavelength, and reaction time on both of the toluene conversion and selectivity to products was examined. The obtained results are presented in Table 1.

First, the photooxidation of toluene was examined under blue LED irradiation (Table 1, entries 1–5); When the toluene photooxidation was carried out in the presence of 0.02 mmol TBATB under blue LED irradiation in CH<sub>3</sub>CN, 58 % conversion and 50 % benzaldehyde were obtained in 6 h (Table 1, entry 1). Although with increasing the reaction time from 6 to 8, the conversion of toluene increased to 73 %, the selectivity to benzaldehyde decreased due to over oxidation of benzaldehyde to benzoic acid (Table 1, entry 2). When the photooxidation of toluene was carried out over 0.04 mmol TBATB instead of 0.02 mmol, the toluene conversion and yield of benzaldehyde were respectively 61 % and 51 % after 3 h (Table 1, entry 3) which was similar to the obtained result over 0.02 mmol TBATB in 6 h (Table1, entry 1). It revealed that the conversion rate of toluene to benzaldehyde in CH<sub>3</sub>CN was faster in the presence of higher amount of TBATB (0.04 mmol) as compared to lower amount of it (0.02 mmol) as demonstrated by comparison of entry 1 with 3 in Table 1. In the following, the toluene photooxidation was investigated under blue LED irradiation in EtOAc (Table 1, entries 4–5). The obtained results show that changing the solvent from CH<sub>3</sub>CN to

Aerobic vis	sible light	oxidation	of t	oluene	over	TBATB.
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CH <sub>3</sub> LED, TBATB Solvent (10 m O <sub>2</sub> -balloon, rt	OH	H O	HO O	
1 mmol	А	в	С	
Entry	TBATB	(mmol)		5
1	0.02			,
2	0.02			(

1 mmol	A B C	;						
Entry	TBATB (mmol)	Solvent	LED	Time (h)	A (%) <sup>d</sup>	B (%) <sup>d</sup>	C (%) <sup>d</sup>	Conversion (%) <sup>d</sup>
1	0.02	CH <sub>3</sub> CN	Blue	6	5	50	3	58
2	0.02	CH <sub>3</sub> CN	Blue	8	8	51	14	73
3	0.04	CH <sub>3</sub> CN	Blue	3	9	51	1	61
4	0.02	EtOAc	Blue	8	3	19	52	74
5	0.04	EtOAc	Blue	8	3	24	41	68
6	0.02	CH <sub>3</sub> CN	Violet	8	9	51	23	83
7	0.04	CH <sub>3</sub> CN	Violet	3	8	54	22	84
8	0.02	EtOAc	Violet	8	2	10	75	87
9	0.02	EtOAc	Violet	10	2	10	75	87
10	0.04	EtOAc	Violet	8	2	4	74	80
11	0.01	EtOAc	Violet	8	0	11	25	36
12	0.02	$CH_2Cl_2$	Violet	8	7	17	6	30
13	0.02	$H_2O$	Violet	8	35	15	26	76
14	0	EtOAc	Violet	8	0	0	0	0
15 <sup>a</sup>	0.02	EtOAc	-	8	0	0	0	0
16 <sup>b</sup>	0.02	EtOAc	Violet	8	0	0	0	0
17 <sup>c</sup>	0.02	EtOAc	Violet	8	0	16	40	56
18 <sup>c</sup>	0.04	EtOAc	Violet	8	14	0	60	74

Photooxidation of toluene.

<sup>a</sup> In a dark room.

<sup>b</sup> Under an argon atmosphere.

<sup>c</sup> 2 mmol toluene.

 $^{\rm d}\,$  GC yield.

EtOAc resulted in no significant effect on toluene conversion under irradiation of blue LED, but the selectivity to benzoic acid was further in EtOAc as compared to CH<sub>3</sub>CN as demonstrated by comparison of entry 2 with entry 4 in Table 1. Increasing the amount of TBATB from 0.02 to 0.04 mmol did not offer considerable progress on the toluene conversion under irradiation of blue LED in EtOAc (Table 1, entries 4 and 5). Therefore, in the photooxidation of toluene under blue LED irradiation in EtOAc, the best result (74 % toluene conversion and 52 % benzoic acid) was obtained over 0.02 mmol TBATB in 8 h (Table 1, entry 4). A comparison of the results obtained in the photooxidation of toluene over TBATB under blue irradiation indicated that the EtOAc was the best solvent to produce benzoic acid, and CH3CN was the best one to produce benzaldehyde (Table 1, entries 1-5).

Next, toluene photooxidation was examined under violet LED irradiation in CH<sub>3</sub>CN (Table 1, entries 6–7). The violet LED irradiation compared to blue LED irradiation has a more accelerating effect on the conversion rate of toluene, as demonstrated by comparison of entry 2 with 6 in Table 1, because the wavelengths of the violet LED were

shorter than the blue ones. When the photocatalytic oxidation of toluene over TBATB under violet LED irradiation was examined in EtOAc (Table 1, entries 8-10), it was found that toluene can be oxidized to benzoic acid more efficiently in EtOAc under violet LED irradiation compare to blue LED irradiation as demonstrated by comparison of entry 4 with 8 in Table 1 (Fig. 1) [21,22,25].

With increasing the reaction time from 8 to 10 h, no change was observed in both of the toluene conversion and selectivity of products (Table 1, entry 9). On the other hand, photooxidation of toluene over 0.01 mmol TBATB led to a decrease in the toluene conversion (Table 1, entry 11). The best result (87 % toluene conversion and 75 % benzoic acid) was obtained over 0.02 mmol TBATB in EtOAc under violet LED irradiation after 8 h (Table 1, entry 8). Therefore, 0.02 mmol TBATB, EtOAc, and violet LED were selected as the optimized conditions for the photooxidation of toluene to benzoic acid (Table 1, entry 8). It was found that all of the factors (such as wavelength, type of solvent, amount of TBATB, and reaction time) together influence the tunable photooxidation of toluene. By adjusting these factors, the reactions conduct to



Fig. 1. Aerobic Photooxidation of 1 mmol toluene over 0.02 mmol TBATB in 10 mL CH<sub>3</sub>CN or EtOAc under irradiation of A) violet or B) blue LED in 8 h.

benzaldehyde or benzoic acid. It seems that the toluene photooxidation tunability over TBATB depends on the rate of oxidation: Parameters such as wavelength, type of solvent, amount of TBATB, and reaction time effect on the rate of transformation of toluene to benzaldehyde or benzoic acid. The longer wavelengths (blue LED irradiation, 460 nm), CH<sub>3</sub>CN, higher amount of photocatalyst (0.04 mmol), and short reaction time (3 h) led to tunable photooxidation of toluene to benzaldehyde (Table 1, entry 3). On the other hand, the shorter wavelengths (violet LED irradiation, 400 nm), EtOAc, lower amount of photocatalyst (0.02 mmol), and long reaction time (8 h) led to over oxidation of toluene to benzoic acid (Table 1, entry 8).

Subsequently, the effect of solvents such as  $CH_2Cl_2$  and  $H_2O$  on the aerobic photooxidation of toluene was examined in the optimized reaction condition (Table 1, entries 12 and 13); the photooxidation of toluene in  $CH_2Cl_2$  resulted in a low conversion of toluene (Table 1, entry 12). A mixture of benzyl alcohol, benzaldehyde, and benzoic acid was obtained in the photooxidation of toluene in  $H_2O$  (Table 1, entry 13). On the other hand, No oxidation product was obtained in the absence of TBATB as a photocatalyst, LED as light source, and oxygen as oxidant (Table 1, entries 14–16); it can be concluded that the TBATB, LED, and oxygen play essential roles in the toluene oxidation.

When the photooxidation was conducted for 2 mmol toluene using the optimum reaction condition, 56 % toluene conversion and 40 % benzoic acid were obtained (Table 1, entry 17). On the other hand, 2 mmol of toluene was successfully oxidized in high conversion (74 %) and high yield to benzoic acid

(60 %) in the presence of 0.04 mmol TBATB in 8 h (Table 1, entry 18).

The results revealed that CH<sub>3</sub>CN, 0.04 mmol TBATB, and blue (460 nm) LED irradiation (**method B**) were the best conditions for the selective photooxidation of toluene to benzaldehyde. On the other hand, EtOAc, 0.02 mmol TBATB, and violet (400 nm) LED irradiation (**method A**) were the best conditions for the selective photooxidation of toluene to benzoic acid. Therefore, **methods A and B** were separately used to convert toluene derivatives to benzoic acid and benzaldehyde, respectively (Table 2).

High yield of p-methoxybenzoic acid (95%) with a turnover number (TON) of 50 was obtained in the photooxidation of p-methoxytoluene under method A (Table 2, entry 1). On the other hand, 50 % pmethoxybenzaldehyde with a TON of 12.5 was generated in 3 h under method B (Table 2, entry 2). In order to increase the transformation of p-methoxytoluene into p-methoxybenzaldehyde, method C (CH<sub>3</sub>CN, 0.04 mmol TBATB, and royal blue LED irradiation with 430 nm wavelength) was examined. Royal blue LED (430 nm) was used instead of blue LED in method C. Remarkably, 75 % p-methoxybenzaldehyde without any production of p-methoxybenzoic acid and with a TON of 18.8 was obtained in 3 h under method C (Table 2, entry 3). In the photooxidation of 1 mmol ethylbenzene, high yield of acetophenone (95 %) was obtained after 10 h under method A (Table 2, entry 4). Replacement of the violet LED to blue and royal blue LED resulted in a decrease in photooxidation of ethyl benzene; 72 and 79 % acetophenone was obtained after 25 h, respectively, under method B and C (Table 2, entries 5 and 6). Photooxidation of 2 mmol ethylbenzene resulted in 85 % acetophenone with a TON of 45 in 25 h under method A (Table 2, entry 7). 1-Bromo-4-ethylbenzene was converted into the p-bromoacetophenone in high yield (89 and 96 %) with high TONs (23.3, 25, and 50) under method B, C, and A (Table 2, entries 8-10). Fluorene was converted into fluorenone in high yields 80 and 65 % after 47 h under method A and B, respectively (Table 2, entries 12 and 13). It should be mentioned that the fluorene was oxidized to the fluorenone with a high TON of 44 under method A (Table 2, entry 12). There were reports in which fluorene was converted into the fluorenone over the high amount of metal catalyst Co-Cu (100 mg) at 110 °C [43], V<sub>2</sub>O<sub>5</sub>-Fe<sub>2</sub>O<sub>3</sub> at high temperature (350 °C) [44], and metal catalyst CoCu-H (50 mg) at 90 °C [45]; therefore the photooxidation of fluorene to fluorenone in high yield (80 %) over a low amount of TBATB as a metal-free photocatalyst

under mild condition (LED irradiation) has great importance. In the photooxidation of p-toluic acid, 40 % terephthalic acid was produced after 21-60 h under method A (Table 2, entries 14 and 15). This report has great importance compare to the reports in which terephthalic acid was obtained from oxidation of p-toluic acid over metal catalysts at high temperature [46,47]. In the photooxidation of o-xylene, 97 % o-toluic acid was generated with a high TON 50 after 48 h under method A (Table 2, entry 16). 44 % o- tolualdehyde was obtained after 23 h under method B (Table 2, entry 17). Diphenyl acetic acid converted into benzophenone in high yields 96 % with high TONs (50 and 25) under methods A, B, and C (Table 2, entries 19-21). p-Iodotoluene was oxidized to the p-iodobenzoic acid (89 %) after 45 h under method A (Table 2, entry 22). On the other hand, photooxidation of p-iodotoluene led to the production of only 5% p-iodotoluene under method C after 24 and 48 h (Table 2, entries 23 and 24). It seems that the photooxidation of p-iodotoluene was not proceeding well in CH<sub>3</sub>CN. In the photooxidation of p-bromotoluene, a good yield (43 %) of p-bromobenzoic acid was obtained after 12 h under method A (Table 2, entry 25). The produced p-bromobenzoic acid increased from 43 to 50 %, with an increase in the reaction time from 12 to 28 h (Table 2, entry 26). Also, 67 % of p-bromobenzaldehyde was achieved after 24 h under method C (Table 2, entry 27).

p-Chlorotoluene compare to the p-bromotoluene exhibited a lower tendency to oxidize over TBATB: a mixture of p-chlorobenzoic acid (12%) and p-chlorobenzaldehyde (6%) was obtained in the photooxidation of p-chlorotoluene under violet LED irradiation in EtOAc after 24 h (Table 2, entry 28). It can be concluded that the presence of electron-withdrawing groups on toluene ring leads to lower reactivity of sub-strate and a lower product yield. In the photooxidation of p-chlorotoluene 21 and 33% p-bromobenzaldehyde was respectively generated under **methods B** and **C** in 18 h (Table 2, entries 29 and 30). The presence of the nitro group at the para or ortho position of the toluene ring resulted in a decelerating influence on the photooxidation reaction (Table 2, entries 31–33).

o-Nitrotoluene, compared to p-nitrotoluene, exhibited no reactivity in photooxidation reaction. Photooxidation of o-nitrotoluene under **methods A, B**, and **C** resulted in no conversion to oxidation products (Table 2, entries 34–36); it can be caused by the steric hindrance of nitro substitution near the active site. Photooxidation of p-cresol and p-toluidine over TBATB resulted in no conversion (Table 2, entries 37–40); it seems that reactions between the phenolic or aniline compounds and bromine lead to inactivation of bromine [42]. Photooxidation of diphenylmethane over TBATB resulted in high yield of benzophenone (Table 2, entries 41–42).

Then photooxidation of adamantane as an aliphatic hydrocarbon was investigated over TBATB. Only 13 % 1-adamantole was obtained in the photooxidation of adamantane after 48 h under **method A** and **C** (Table 2, entries 43 and 44). It can be concluded that compared to aromatic hydrocarbons, aliphatic hydrocarbons show a low tendency to oxidize.

Finally, a plausible mechanism was suggested for the aerobic visible light oxidation of toluene over TBATB (Scheme 2). The yellow coloration of the solution containing TBATB offers that bromine is initially generated from TBATB [21]. Also, instantly color disappearing of the TBATB solution after the addition of cresols as phenolic compound confirms this hypothesis. Toluene can react with bromine radicals produced via photodissociation of Br2 to afford benzyl radical 1 and hydrobromic acid (HBr) [22]. HBr subsequently can be transformed into the bromo radical upon an aerobic photooxidation process [22,25,48]. Benzyl radical 1 can abstract molecular oxygen (exothermic by  $\Delta$ H298  $= -93.4 \pm 2.5$  kJ mol-1) to form peroxy radical 2 [22,49–52]. The peroxy radical 2 abstracts hydrogen to produce benzyl hydroperoxide 3 [22]. At higher concentrations of benzyl hydroperoxide 3, the self-reaction (R1) is considerably more probable than other reactions [52]. Therefore, hydroperoxybenzyl radical 4 and benzyloxy radical 5 are generated which subsequently transform into benzaldehyde (R2)

# Table 2

Photooxidation of toluenes derivatives over TBATB.

	Method A: Violet LED (400 nm), TBATB (0.02 mmol) EtOAc (10 mL), $O_2$ -balloon, rt	
Substrate _ (1 mmol)	Method B: Blue LED (460 nm), TBATB (0.04 mmol) CH <sub>3</sub> CN (10 mL), O <sub>2</sub> -balloon, rt	Budat
	Method C: Royal blue LED (430 nm), TBATB (0.04 mmol) CH <sub>3</sub> CN (10 mL), O <sub>2</sub> -balloon, rt	

Entry	Substrate	Method	Product	Time (h)	Conversion (%)	Product GC vield (%)	Isolated vield (%)	Selectivity	TON <sup>d</sup>
	Substitute	methou	Trouter				isolated field (70)	(%)	
1		Α	MeO	12	100	100	95	100	50
2	CH <sub>3</sub>	В	Meo	3	50	50	45	100	12.5
3	moo	С	мео	3	75	75	70	100	18.8
4		Α	СН3	10	100	100	95	100	50
5	CH <sub>2</sub> CH <sub>3</sub>	В	СНа	25	78	78	72	100	19.5
6		С	СН3	25	85	85	79	100	21.25
7 <sup>a</sup>		Α	CH3	25	90	90	85	100	45
8		Α	Br CH <sub>3</sub>	23	100	100	96	100	50
9	Br CH <sub>2</sub> CH <sub>3</sub>	В	CH <sub>3</sub>	23	93	93	89	100	23.3
10		С	СН3	23	100	100	96	100	25
11		Α		18	62	62	55	100	31
12		Α		47	88	88	80	100	44
13		В		47	73	73	65	100	18.3
14	CH3	Α	СООН	21	-	_	40	100	20*
15	ноос	Α	HOOC	60	-	-	40	100	20*
16		Α	COOH CH <sub>3</sub>	48	100	100	97	100	50
17	CH <sub>3</sub> CH <sub>3</sub>	В	CHO CH <sub>3</sub>	23	44	44	40	100	11
18 <sup>b</sup>		С	CHO CH <sub>3</sub>	23	46	37	33	80	9.3
19		Α		18	100	100	96	100	50
20	СООН	В		23	100	100	96	100	25
21		С		23	100	100	96	100	25
22		Α	СООН	45	89	89	80	100	44.5
23	CH <sub>3</sub>	С	СНО	24	10	10	5	100	2.5
24	F ∽	С	СНО	48	10	10	5	100	2.5
25	CH3	Α	Br	12	50	50	43	100	25
26	Br	Α	СООН	28	57	57	50	100	28.5
27		С	01	24	67	67	60	100 (continued on r	16.8 next page)

#### Table 2 (continued)

	Method A: Violet LED (400 nm), TBATB (0.02 mmol) EtOAc (10 mL), O <sub>2</sub> -balloon, rt								
Substrate (1 mmol)	Method B: Blue LED CH <sub>3</sub> CN (10 mL), O <sub>2</sub> -t	(460 nm), TBATB ( balloon, rt	(0.04 mmol)						
	Method C: Royal blue LED (430 nm), TBATB (0.04 mmol) CH <sub>3</sub> CN (10 mL), O <sub>2</sub> -balloon, rt			duct					
Entry	Substrate	Method	Product	Time (h)	Conversion (%)	Product GC yield (%)	Isolated yield (%)	Selectivity (%)	TON <sup>d</sup>
			СНО						
28 <sup>c</sup>		Α	СООН	24	18	12	-	67	6
29	CH <sub>3</sub>	В	СНО	18	21	21	17	100	5.3
30	Ci	С	СНО	18	33	33	29	100	8.3
31		Α	O <sub>2</sub> N CHO	24	10	10	2	100	5
32	O2N CH3	В	O <sub>2</sub> N CHO	48	7	7	-	100	1.8
33		С	СНО	48	14	14	6	100	3.5
34		Α	0 <sub>2</sub> N <sup>2</sup>	18	0	0	0	_	0
35	CH <sub>3</sub>	В	-	18	0	0	0	-	0
36	NO <sub>2</sub>	С	-	18	0	0	0	-	0
37	CH3	Α	-	24	0	0	0	-	0
38		В	-	24	0	0	0	-	0
39	HO CH3	Α	-	24	0	0	0	-	0
40	H <sub>2</sub> N	В	-	24	0	0	0	-	0
41	$\sim \sim \sim$	Α		12	100	100	98	100	50
42	$\bigcirc$ $\bigcirc$	С	0°0	12	100	100	98	100	25
43	$\frown$	Α	OH C	48	13	13	-	100	6.5
44	H	С	- OH	48	13	13	-	100	3.3

<sup>a</sup> 2 mmol substrate, 0.04 mmol TBATB.

<sup>b</sup> 9 % of o-toluic acid was produced.

<sup>c</sup> 6 % of p-chlorobenzaldehyde was produced.

<sup>d</sup> TON = mmol of products (achieved by GC) divided by mmol of TBATB.

\* mmol of isolated products divided by mmol of TBATB.

and benzyl alcohol, respectively (R1 + R2 are exothermic reactions by  $\Delta H_{298} = -55.7$  kJ mol<sup>-1</sup> and  $\Delta G = -144.3$  kJ mol<sup>-1</sup>) [20,52,53]. Benzyl alcohol can react with a bromo radical to generate benzylic radical 6 and HBr. Then benzylic radical 6 can abstract oxygen to produce peroxy radical 7 which traps hydrogen to generate hydroperoxide 8 [21,24,26, 48,49,54]. The hydroperoxide 8 transforms into benzaldehyde with the selective CO— bond cleavage [26]. The aldehyde C—H bond in benzaldehyde can be dissociated by free radicals [55], which can be generated in the photooxidation reaction; therefore, 9 can be produced. The abstraction of O<sub>2</sub> by 9 resulted in the generation of 10, which subsequently converts into perbenzoic acid 11 through hydrogen trapping [55]. Finally, benzoic acid can be produced via non-radical Baeyer–Villiger-type oxidation reaction [55].

In several researches in which bromo sources were used as photocatalyst, EtOAc was introduced as the best solvent to conduct photooxidation of toluenes and benzyl alcohols to the benzoic acids [21,25,28, 48]. On the other hand, CH<sub>3</sub>CN known as the best solvent to conduct photooxidation of toluenes and benzyl alcohols to benzaldehydes [27, 54], but there are no explanation about this phenomenon. It may be caused by higher tendency of free radicals to hydrogen atom abstraction from C—H bonds of benzaldehyde in EtOAc compare to CH<sub>3</sub>CN [56]. Therefore, radical species **9** was easily formed in EtOAc compare to CH<sub>3</sub>CN. To support the possible dissociation of the toluene C—H bond, trapping  $O_2$  by the radical **1**, and generation of benzyl hydroperoxide **3**, photocatalytic oxidation of cumene in the presence of TBATB in EtOAc under violet LED irradiation was examined in 3 h (Scheme 3). The formation of cumene hydroperoxide was confirmed by <sup>1</sup>H NMR and <sup>13</sup>C NMR analysis (SI).

## 4. Conclusion

Herein, we reported on an efficient visible light active photocatalytic system which can be utilized to transform toluene, its derivatives, and methyl arenes into the corresponding benzaldehydes, benzoic acids and ketones in good to high yield. It was found that the selectivity of the oxidation products in this photocatalytic system can be influenced by changing the irradiation wavelengths (from blue (460 nm) to violet (400 nm)) and solvents (from CH<sub>3</sub>CN to EtOAc). Toluene was successfully converted into the benzoic acid in high conversion (87 %), and high selectivity (86 %) under violet LED irradiation (400 nm) in EtOAc. However, toluene was oxidized to benzaldehyde as in good conversion (61 %), and high selectivity (84 %) under blue LED irradiation (460 nm) in CH<sub>3</sub>CN. EtOAc was introduced as a suitable solvent for the conversion of toluene to benzoic acid. CH<sub>3</sub>CN was considered to be an appropriate solvent in the transformation of toluene to benzaldehyde under blue LED



Scheme 2. Probable mechanism for aerobic photooxidation of toluene.



Scheme 3. Photocatalytic aerobic oxidation of cumene.

irradiation. All of the LED wavelength radiation, dosage of TBATB, type of solvent, and the reaction time could be effected the reaction conversion and products selectivity. Finally, dissociation of the toluene C—H bond, trapping  $O_2$  by the obtained radical species, and generation of benzyl hydroperoxide species was confirmed via photocatalytic oxidation of cumene over TBATB. Our mechanistic studies revealed that the selective visible light oxidation of toluene could be following a benzyl peroxy radical intermediate.

#### Author statement

Atefeh Mardani: Methodology, Data Curation, Writing - Original Draft, Writing - Review & Editing.

Foad Kazemi: Conceptualization, Supervision, Project administration, Writing - Review & Editing, Investigation.

Babak Kaboudin: Writing - Review & Editing, Validation.

#### Data availability

Data will be made available on request.

#### **Declaration of Competing Interest**

The authors report no declarations of interest.

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# Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jphotochem.2021. 113301.

#### References

- [1] K. Cai, S.-Y. Lv, L.-N. Song, L. Chen, J. He, P. Chen, C.-T. Au, S.-F. Yin, Facile preparation of ultrathin Bi<sub>2</sub>MoO<sub>6</sub> nanosheets for photocatalytic oxidation of toluene to benzaldehyde under visible light irradiation, J. Solid State Chem. 269 (2019) 145–150.
- [2] X. Wang, G. Wu, F. Wang, H. Liu, T. Jin, Solvent-free selective oxidation of toluene with O<sub>2</sub> catalysed by anion modified mesoporous mixed oxides with high thermal stability, Catal. Commun. 98 (2017) 107–111.
- [3] D. Xia, W. Xu, L. Hu, C. He, D.Y. Leung, W. Wang, P.K. Wong, Synergistically catalytic oxidation of toluene over Mn modified g-C3N4/ZSM-4 under vacuum UV irradiation, J. Hazard. Mater. 349 (2018) 91–100.

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- [4] M. Aydın, E.B. Aydın, M.K. Sezgintürk, Electrochemical immunosensor for CDH22 biomarker based on benzaldehyde substituted poly (phosphazene) modified disposable ITO electrode: a new fabrication strategy for biosensors, Biosens. Bioelectron. 126 (2019) 230–239.
- [5] F.C. Binks, G. Cavalli, M. Henningsen, B.J. Howlin, I. Hamerton, On the use of benzaldehyde to improve the storage stability of one-pot, epoxy ionic liquid formulations, Eur. Polym. J. 112 (2019) 126–136.
- [6] B. Shrivastava, O. Sharma, P. Sharma, J. Singh, Synthesis, characterization and antimicrobial evaluation of novel azole based (Benzoic Acid) derivatives, Asian J. Pharm. Sci. 5 (2019) 368–372.
- [7] S. Gatadi, J. Gour, M. Shukla, G. Kaul, A. Dasgupta, Y. Madhavi, S. Chopra, S. Nanduri, Synthesis and evaluation of new 4-oxoquinazolin-3 (4H)-yl) benzoic acid and benzamide derivatives as potent antibacterial agents effective against multidrug resistant Staphylococcus aureus, Bioorg. Chem. 83 (2019) 569–579.
- [8] T. Coleman, R.R. Chao, J.J. De Voss, S.G. Bell, The importance of the benzoic acid carboxylate moiety for substrate recognition by CYP199A4 from Rhodopseudomonas palustris HaA2, Biochim. Biophys. Acta (BBA)-Proteins Proteomics 1864 (2016) 667–675.
- [9] B. Yuan, B. Zhang, Z. Wang, S. Lu, J. Li, Y. Liu, C. Li, Photocatalytic aerobic oxidation of toluene and its derivatives to aldehydes on Pd/Bi<sub>2</sub>WO<sub>6</sub>, Chin. J. Catal. 38 (2017) 440–446.
- [10] W. Deng, Y.-p. Wan, H. Jiang, W.-P. Luo, Z. Tan, Q. Jiang, C.-C. Guo, Solvent-free aerobic oxidation of toluene over metalloporphyrin/NHPI/CTAB: synergy and mechanism, Catal. Lett. 144 (2014) 333–339.
- [11] G. Shi, S. Xu, Y. Bao, J. Xu, Y. Liang, Selective aerobic oxidation of toluene to benzaldehyde on immobilized CoOx on SiO<sub>2</sub> catalyst in the presence of Nhydroxyphthalimide and hexafluoropropan-2-ol, Catal. Commun. 123 (2019) 73–78.
- [12] M. Huda, K. Minamisawa, T. Tsukamoto, M. Tanabe, K. Yamamoto, Aerobic toluene oxidation catalyzed by subnano metal particles, Angew. Chem. Int. Ed. 58 (2019) 1002–1006.
- [13] X.-H. Li, X. Wang, M. Antonietti, Solvent-free and metal-free oxidation of toluene using O2 and g-C3N4 with nanopores: nanostructure boosts the catalytic selectivity, ACS Catal. 2 (2012) 2082–2086.
- [14] A. Mardani, Z. Mohamadnia, F. Kazemi, Coagulation performance of cationic polyelectrolyte/TiO<sub>2</sub> nanocomposites prepared under LED irradiation, J. Appl. Polym. Sci. 137 (37) (2020) 49113–49126.
- [15] A. Mardani, F. Kazemi, Z. Mohamadnia, Polyelectrolyte-controlled visible light catalytic reduction of nitrobenzene, Polym. Adv. Technol. 32 (2) (2021) 484–496.
- [16] G.R. Bertolini, L.R. Pizzio, A. Kubacka, M.J. Muñoz-Batista, M. Fernández-García, Composite H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>-TiO<sub>2</sub> catalysts for toluene selective photo-oxidation, Appl. Catal. B 225 (2018) 100–109.
- [17] M.J. Muñoz-Batista, G.R. Bertolini, C.I. Cabello, R. Luque, E. Rodríguez-Castellón, A. Kubacka, M. Fernández-García, Novel (NH<sub>4</sub>)<sub>4</sub>[NiMo<sub>6</sub>O<sub>24</sub>H<sub>6</sub>]· 5H<sub>2</sub>O-TiO<sub>2</sub> composite system: photo-oxidation of toluene under UV and sunlight-type illumination, Appl. Catal. B 238 (2018) 381–392.
- [18] M.D. Hernández-Alonso, I. Tejedor-Tejedor, J.M. Coronado, M.A. Anderson, Operando FTIR study of the photocatalytic oxidation of methylcyclohexane and toluene in air over TiO<sub>2</sub>–ZrO<sub>2</sub> thin films: influence of the aromaticity of the target molecule on deactivation, Appl. Catal. B 101 (2011) 283–293.
- [19] S. Ouidri, H. Khalaf, Synthesis of benzaldehyde from toluene by a photocatalytic oxidation using TiO<sub>2</sub>-pillared clays, J. Photochem. Photobiol. A 207 (2009) 268–273.
- [20] N. Tada, K. Hattori, T. Nobuta, T. Miura, A. Itoh, Facile aerobic photooxidation of methyl group in the aromatic nucleus in the presence of an organocatalyst under VIS irradiation, Green Chem. 13 (2011) 1669–1671.
- [21] A. Itoh, S. Hashimoto, Y. Masaki, Facile aerobic photooxidation of alcohols in the presence of catalytic lithium bromide, Synlett 17 (2005) 2639–2640.
- [22] A. Itoh, S. Hashimoto, T. Kodama, Y. Masaki, Aerobic photooxidation of methyl group at aromatic nucleus with LiBr, Synlett 13 (2005) 2107–2109.
- [23] S.-i. Hirashima, S. Hashimoto, Y. Masaki, A. Itoh, Aerobic photo-oxidation of alcohols in the presence of a catalytic inorganic bromo source, Tetrahedron 62 (2006) 7887–7891.
- [24] K. Kuwabara, A. Itoh, Facile aerobic photooxidation of alcohols in the presence of catalytic N-bromosuccinimide, Synthesis 12 (2006) 1949–1952.
- [25] S.-i. Hirashima, A. Itoh, Aerobic oxidation of alcohols under visible light irradiation of fluorescent lamp, Green Chem. 9 (2007) 318–320.
- [26] Y.-M. Zhong, H.-C. Ma, J.-X. Wang, X.-J. Jia, W.-F. Li, Z.-Q. Lei, AlBr<sub>3</sub>. 6H<sub>2</sub>O catalyzed oxidation of benzylic alcohols, Catal. Sci. Technol. 1 (2011) 927–931.
- [27] S. Tripathi, S.N. Singh, L.D.S. Yadav, Visible light photocatalysis with CBr4: a highly selective aerobic photooxidation of methylarenes to aldehydes, RSC Adv. 6 (2016) 14547–14551.
- [28] T. Sugai, A. Itoh, Aerobic photo-oxidation in the presence of catalytic allylbromide, Tetrahedron Lett. 48 (2007) 2931–2934.
- [29] T. Sugai, A. Itoh, Aerobic oxidation under visible light irradiation of a fluorescent lamp with a combination of carbon tetrabromide and triphenyl phosphine, Tetrahedron Lett. 48 (2007) 9096–9099.

- [30] L.Q. Wu, C.G. Yang, Y.F. Wu, L.M. Yang, Synthesis of 6-bromocoumarins using tetrabutylammonium tribromide as a selective brominating agent and an efficient generator of HBr, J. Chin. Chem. Soc. 56 (2009) 606–608.
- [31] U. Bora, G. Bose, M.K. Chaudhuri, S.S. Dhar, R. Gopinath, A.T. Khan, B.K. Patel, Regioselective bromination of organic substrates by tetrabutylammonium bromide promoted by V<sub>2</sub>O<sub>5</sub>-H<sub>2</sub>O<sub>2</sub>: an environmentally favorable synthetic protocol, Org. Lett. 2 (2000) 247–249.
- [32] M.K. Chaudhuri, A.T. Khan, B.K. Patel, D. Dey, W. Kharmawophlang, T. Lakshmiprabha, G.C. Mandal, An environmentally benign synthesis of organic ammonium tribromides (OATB) and bromination of selected organic substrates by tetrabutylammonium tribromide (TBATB), Tetrahedron Lett. 39 (1998) 8163–8166.
- [33] R. Karmaker, N.B. Kuotsu, A. Ganguly, N. Guchhait, U.B. Sinha, A theoretical and experimental study on the effect of cationic moiety of quaternary ammonium tribromides in bromination reactions, Chem. Phys. Lett. 711 (2018) 118–126.
- [34] I. Saikia, A.J. Borah, P. Phukan, Use of bromine and bromo-organic compounds in organic synthesis, Chem. Rev. 116 (2016) 6837–7042.
- [35] E. Mondal, G. Bose, A.T. Khan, An expedient and efficient method for the cleavage of dithioacetals to the corresponding carbonyl compounds using organic ammonium tribromide (OATB), Synlett 6 (2001) 0785–0786.
- [36] S. Naik, R. Gopinath, B.K. Patel, Tetrabutylammonium tribromide (TBATB)promoted tetrahydropyranylation/depyranylation of alcohols, Tetrahedron Lett. 42 (2001) 7679–7681.
- [37] S. Naik, V. Kavala, R. Gopinath, B.K. Patel, Tetrabutylammonium tribromide mediated condensation of carboxylic acids with alcohols, Arkivoc 1 (2006) 119–127.
- [38] R. Gopinath, B.K. Patel, Tetrabutylammonium tribromide (TBATB)– MeOH: an efficient chemoselective reagent for the cleavage of tert-butyldimethylsilyl (TBDMS) ethers, Org. Lett. 2 (2000) 4177–4180.
- [39] M. Baghmar, P.K. Sharma, Kinetics and mechanism of oxidation of aliphatic alcohols by tetrabutylammonium tribromide, J. Chem. Sci. 113 (2001) 139–146.
- [40] J. Gosain, P.K. Sharma, Kinetics and mechanism of the oxidation of some vicinal and non-vicinal diols by tetrabutylammonium tribromide, J. Chem. Sci. 115 (2003) 135–145.
- [41] R. Razeghi, F. Kazemi, N. Nikfarjam, Y. Shariati, B. Kaboudin, Visible photoinduced catalyst-free polymerization via in situ prepared dibromide, Eur. Polym. J. 144 (2021), 110195.
- [42] A. Mardani, M. Heshami, Y. Shariati, F. Kazemi, M.A. Kakroudi, B. Kaboudin, A tunable synthesis of either benzaldehyde or benzoic acid through blue-violet LED irradiation using TBATB, J. Photochem. Photobiol. 389 (2019) 112220–112242.
- [43] J. Luo, K. Xuan, Y. Wang, F. Li, F. Wang, Y. Pu, L. Li, N. Zhao, F. Xiao, Aerobic oxidation of fluorene to fluorenone over Co–Cu bimetal oxides, New J. Chem. 43 (2019) 8428–8438.
- [44] F. Majunke, H. Borchert, M. Baerns, Catalytic Oxidation of Fluorene to 9-Fluorenone-Development and Characterization of Catalysts, Studies in Surface Science and Catalysis, Elsevier, 1993, pp. 707–717.
- [45] J. Luo, Y. Wang, F. Wang, F. Li, L. Li, N. Zhao, F. Xiao, Aerobic oxidation of fluorene to fluorenone over copper-doped Co<sub>3</sub>O<sub>4</sub> with a high specific surface area, ACS Sustain. Chem. Eng. 8 (2020) 2568–2576.
- [46] M.A. Betiha, N.G. Kandile, A.M. Badawi, S.M. Solyman, A.S. Afify, Oxidation of ptoluic acid to terephthalic acid via a bromine-free process using nano manganese and manganese-copper mixed oxides, New J. Chem. 42 (2018) 6343–6353.
- [47] Y. Xiao, W. Luo, X. Zhang, C. Guo, Q. Liu, G. Jiang, Q. Li, Aerobic oxidation of ptoluic acid to terephthalic acid over T(p-Cl) PPMnCl/Co(OAc)<sub>2</sub> under moderate conditions, Catal. Lett. 134 (2010) 155–161.
- [48] A. Itoh, S. Hashimoto, K. Kuwabara, T. Kodama, Y. Masaki, Facile solar oxidation of alcohols with molecular oxygen, Green Chem. 7 (2005) 830–832.
- [49] K.R. Barnard, V.R. Bright, R.J. Enright, K.M. Fahy, A.C. Liu, P.E. Hoggard, Heterogeneous catalysis by tetraethylammonium tetrachloroferrate of the photooxidation of toluene by visible and near-UV light, Catalysts 8 (2018) 79.
- [50] J. Ma, J. Yu, W. Chen, A. Zeng, The effect of water on the oxidation of toluene catalyzed by molybdenum manganese complex oxide, Catal. Lett. 146 (2016) 1600–1610.
- [51] Y.-R. Luo, Comprehensive Handbook of Chemical Bond Energies, CRC press, 2007.
  [52] L. Sandhiya, H. Zipse, Initiation chemistries in hydrocarbon (Aut) oxidation, Chem. Eur. J. 21 (2015) 14060–14067.
- [53] M.A. Callahan, Water-related Environmental Fate of 129 Priority Pollutants, Office of Water Planning and Standards, Office of Water and Waste Management, 1979.
- [54] S. Gazi, R. Ananthakrishnan, Bromodimethylsulfonium bromide as a potential candidate for photocatalytic selective oxidation of benzylic alcohols using oxygen and visible light, RSC Adv. 2 (2012) 7781–7787.
- [55] M. Sankar, E. Nowicka, E. Carter, D.M. Murphy, D.W. Knight, D. Bethell, G. J. Hutchings, The benzaldehyde oxidation paradox explained by the interception of peroxy radical by benzyl alcohol, Nat. Commun. 5 (2014) 3332.
- [56] L.M. Dorfman, G.E. Adams, Reactivity of the Hydroxyl Radical in Aqueous Solutions, 1973.