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Sustainable Room Temperature Conversion of *p*-Xylene to Terephthalic Acid using Ozone and UV Irradiation.

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The current industrial process utilizes Co/Mn bromides as catalysts to catalyze oxidative conversion of para-xylene to terephthalic acid in acetic acid at high temperatures (>200 °C, air, 15-30 atm.). Decomposition of metallo-catalysts and solvent at high temperatures as well as a later hydropurification process release thousands-million tons of wastewater, global warming gas (CO₂) and ozone depleting gas (CH₃Br) per year to the earth environment, causing global warming, ozone depletion, dramatic climate changes, huge economic loss, and many other environmental problems. Herein, we report an alternative low energy demanding sustainable process for room temperature oxidative conversion of *p*-xylene to terephthalic acid, with 96% TA yield and 98% selectivity, via ozone treatment and concurrent UV irradiation without generation and release of greenhouse gas (CO₂), ozone depleting gases (CH₃Br), and wastewaters, and high energy demanding hydropurification processes. The reaction mechanism involves singlet O(¹D)- and hydroxyl radical-mediated selective C-H functionalization of *p*-xylene.

Introduction

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At present, very few large scale industrial productions of major chemical intermediates are based on low energy-demanding green processes. Terephthalic acid (TA) is one of the largest quantities of key industrial intermediates, and is a raw material for the synthesis of polyethylene terephthalate (PET), polyester, plasticizers, and Kevlar fibers. In 2018, the global production of TA is ~80 million tons per year with a ~5% annual increasing rate per year¹⁻⁵. The polymers derived from TA are widely used in daily life, including soft drink bottles, liquid crystal displays, polyester films/clothes, reinforced glass, bulletproof windows, boats, aircraft, etc. The industrial production of TA is conducted via direct air oxidation of pxylene in corrosive acetic acid at 200 °C in the presence of Co²⁺, Mn²⁺, and bromide catalysts under 15~30 air atmosphere pressure, i.e., the AMOCO-MC process (Figure 1(a)). Due to the high reaction temperature, decarboxylation or "burning" of solvents and products occurs severely, leading to increase in the energy consumption, production cost, generation/emission of global warming gas (CO₂) and ozone depleting gas (CH₃Br), as well as environmental pollution. It was estimated that production of 1 kg TA is accompanied with a loss of 0.05~0.07 kg acetic acid via combustion or burning at high reaction temperatures.^{6.7}, which leads to the generation of ~0.1 ton of global warming CO₂ gas and ~0.000032 ton of ozone-depleting CH₃Br gas per ton of terephthalic

acid7. In the hydropurification process, it was reported that 3~10 tons of wastewater were produced per ton purified TA (pTA)⁸. These values are corresponding to a release of 8 million tons of CO_{2} , ~2.56 kilo-tons of CH₃Br, as well as 240~800 million tons of wastewater to the earth environment per year for annual production of 80 million tons of (ortho-, meta- and para-) phthalic acid. In addition, replenishment of ~5.6 million tons of fresh acetic acid is required per year, which increases the production cost of TA significantly. The wastewater contains various kinds of organic residues, including, acetate, benzoate, terephthalate, p-toluate, etc. 4-Carboxyl benzaldehyde (4-CBA) is the major impurity co-existing with the final terephthalic acid product, and is a terminator in the later polymerization process for the synthesis of PET⁹. In the industrial purification process of crude TA, 4-CBA was catalytically reduced back to p-toluic acid by 0.5 wt% Pd/C under hydrogen atmosphere (>70 atm.) at 270~290 °C in hot water steam¹⁰. Deactivation of Pd catalyst via high-temperature sintering, sulfur and lead poisoning occurs commonly, leading to shortened catalyst lifetime (in general, less than a year)¹⁰⁻¹². In 2000, the demand for the expensive Pd/C catalyst was estimated to be ca. 1000 tons per year^{10,11}. To avoid corrosion by acetic acid and bromide at high temperature, expensive titanium reactors have to be used. Although many efforts have been devoted to developing more energy-saving and greener synthetic conditions to avoid decomposition of metallic catalysts and solvents, the harsh reaction condition and production of several hundred million tons of wastes per year were rarely avoided^{4-6,13,14}. The high energy consumption for the production of crude TA, decomposition of metallo-catalysts, and the release of a huge amount of wastes contribute significantly

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to the global warming, ozone depletion, and environmental soil/atmospheric pollution. In recent years, it was also reported production of pTA by E. coli-assisted conversion of p-xylene or enzymatic conversion of biomass¹⁵⁻¹⁷. However, these bio-based processes are also facing their own problems/challenges, including availability of huge quantities of multiple enzymes, scalability, conversion efficiencies, products production rates, tedious product purification processes, and still have a long way to go before they can compete or replace the current fossil fuel-based industrial AMOCO-MC pTA production process. It is urgently needed to develop a green alternative process for large scale production of pTA and to cut down the energy consumption, resolve these metallo-catalysts associated problems, generation/release of hundreds million tons of wastes/global warming gas/ozone depleting gas every year to the environment, without the need of energy-consuming 4-CBA hydropurification process, and the use of expensive Pd/C catalyst.

In this paper, we report an alternative sustainable process to resolve the above-mentioned pollution problems associated with the metal bromide catalysts-based industrial process for the oxidative conversion of p-xylene to terephthalic acid at room temperature. Our green process utilizes ozone and UV light irradiation to generate highly reactive oxygen atom O(¹D) and hydroxyl radical, which render room temperature oxidative conversion of p-xylene to terephthalic acid become possible.

Results

Inspired by the previous observation that ozone-UV irradiation is able to achieve selective methylene C-H bond oxidation and conversion of cyclohexane to adipic acid¹⁸, we investigate the possibility of using ozone-UV irradiation to oxidatively convert pxylene to terephthalic acid. The industrial nitric acid oxidation method works for the oxidation of cyclohexane to adipic acid, but cannot be applied to oxidize pX to TA, since nitration of aromatic ring occurs preferentially over oxidation of the benzylic protons¹⁹. Likewise, it is not clear whether the ozone-UV irradiation-induced oxidation will occur preferentially at the benzylic C-H bonds over the aromatic C=C and C-H bonds of pX. In addition, the problems involved in the industrial production of pTA are quite different from those associated with the industrial production of adipic acid. Selective C-H bond functionalization of hydrocarbons is known to be very difficult, especially in the absence of any catalysts²⁰⁻²². It still means a lot even if a similar ozone-UV irradiation process can be developed or modified to conquer the above-mentioned problems associated with industrial production of pTA.

In a typical experiment, neat *p*-xylene was bubbled with ozone gas and concurrently irradiated with a 100 W Hg lamp under an exceptionally mild condition, i.e., room temperature (Figure 1(b)). During irradiation, solid precipitates were gradually formed (see optical pictures in supplementary fig. S1). After 20 h irradiation,



Fig. 1. Comparison of processes for production of terephthalic acid.(a) Industrial AMOCO-MC process, and (b) the O₃-UV process.

~80% of p-xylene was converted to solid precipitates, which are composed of p-toluic acid (60 mol%) and TA (20 mol%). Upon bubbling with ozone in the dark for 20 h, 35% p-xylene could also be oxidized and converted to p-toluic acid (30 mol%) with few amounts of TA (5 mol%, Table 1). The structure of p-toluic acid and TA were confirmed by ¹H/ ¹³C NMR spectra as well as single-crystal X-ray crystallography (see the experimental section in supplementary materials and Fig. S2 and S3 for X-ray crystallography of *p*-toluic acid and ethyl terephthalate, respectively). Control experiments show that p-toluic acid and 4-CBA can dissolve in acetonitrile-water (3:2 volume ratio, pH= 4.5) co-solvent, and can be nearly quantitatively oxidized and converted to TA upon ozone treatment and concurrent UV irradiation at room temperature (Table 1). Therefore, it is very likely that coprecipitation of a large quantity of *p*-toluic acid solid with TA solid is due to polarity mismatch and thus poor solubility of p-toluic acid and 4-CBA in neat p-xylene. Precipitation of p-toluic acid and 4-CBA as solids will make these reaction intermediates far less accessible by oxidants. To accelerate oxidation of p-toluic acid and 4-CBA by ozone, singlet O(¹D) atom, and hydroxyl radical (vide infra), we therefore add acetonitrile-water as a co-solvent to p-xylene in order to dissolve and keep the major reaction intermediates (i.e., p-toluic acid and 4-CBA) in the solution phase, rendering them available for further oxidation. After 20 h ozone treatment and UV irradiation of a p-xylene-acetonitrile-water (5:3:2 volume ratio) solution white solid precipitates were still formed, but they are composed of less p-toluic acid (32 mol%) and more TA (65 mol%) in addition to 160 ppm of 4-CBA (see HPLC chromatographs shown in Fig. S4). In a case of p-xylene-acetonitrile-water (1:3:2) solution, we are able to obtain 98% conversion with 96 mol% of TA (that is, ~ 98% selectivity, see Table 1, entry 4) after 26 h O₃-UV irradiation. Since TA is far less soluble in acetonitrile-water co-solvent than p-toluic

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acid and 4-CBA, the solid precipitates collected from the first run of photo irradiation were washed with acetonitrile-water (3:2 v/v, pH= 4.5) to dissolve and remove p-toluic acid and 4-CBA from the solid TA. After 3 times of washing using an equal volume of acetonitrilewater co-solvent, the final washed solid contains 97 mol% of TA and 3 mol% of p-toluic acid and 6 ppm of 4-CBA (see HPLC chromatographs shown in supplementary fig. S4). The final level of 6 ppm 4-CBA is better than that (25 ppm) obtained from the current industrial high temperature hydropurification (0.5 wt% Pd/C, $H_2 > 70$ atm, 270~290 °C in hot water steam) process, but without the need of high energy consumption and the generation of huge amount of wastewater. The washed acetonitrile-water solution is not a waste, and can be recycled. Upon exposure to ozone treatment and UV irradiation, p-toluic acid and 4-CBA in the recycled acetonitrilewater solution can be nearly quantitatively oxidized and converted to solid TA precipitate. By the current low-temperature reaction condition and simple acetonitrile-water solvent washing process, the high energy consuming and costly industrial hydropurification process can be avoided. Meanwhile, the generation of several hundred million tons of wastewater can be substantially reduced. Most importantly, the formation of global warming gas (CO₂) and ozone depleting gas (CH₃Br), which were formed via high temperature decomposition of solvents/products, can be completely avoided.

Under a similar condition, ortho- and meta-xylenes can also be converted to phthalic acid and isophthalic acid, respectively (Table 1). Due to electronic and steric hindrance effects, ortho- and metaxylenes are less easy to be oxidized by ozone, singlet $O(^{1}D)$ atom, and hydroxyl radical (vide infra) as compared to *p*-xylene, leading to relatively lower yields of phthalic acids under the same condition (Table 1). By the same way of ozone treatment and UV irradiation, neat toluene, ethylbenzene and diphenylmethane all can be oxidatively converted to benzoic acid, acetophenone, and benzophenone, respectively, with 75~95% yields at room temperature (Table 2). Benzoate, benzophenone, and acetophenone are food preservative, photo-initiator, and important intermediates in the pharmaceutical industry for the synthesis of various types of medicines/drugs, respectively.

It was reported that photo-irradiation by short UV light ($\lambda < 330$ nm), ozone molecule will decompose into singlet O(¹D) atom and singlet oxygen (¹O₂, ¹\Delta_g) with a quantum yield of 0.79^{23,24}. Control experiments show that prolonged photo irradiation of neat *p*-xylene in the presence of a singlet O₂(¹\Delta_g) photosensitizer at room temperature generates only trace amount of TA, suggesting that singlet O(¹D) atom is probably the key oxidant responsible for the oxidative conversion of *p*-xylene to *p*-toluic acid and terephthalic acid. Singlet O(¹D) atom is known to be able to directly insert into C-H and O-H bonds of hydrocarbons in the gas phase with the conservation of total spin angular momentum^{25,26}. In the current process, it is likely that singlet O(¹D) atom selectively inserts into the benzylic C-H bond of *p*-xylene to generate benzylic alcohol,

followed by second insertion of singlet O(1D) atomevtortianether benzylic C-H bond, the weakest C-H bond among all, to form 1000

Table 1. Substrates scope of oxidative C-H functionalization of xylenes and reaction intermediates. The reactions were carried out either under irradiation using a 100 W Hg lamp (200 mW/cm² at 310 nm) reported first below or in the dark (reported below in parentheses) at room temperature.

Substrat	e Solvent	Products	yield (%)	Time (h)	Total conv (%)	Selectivity of 3 (%)	Mass balance (%)
	neat 2a	CO ₂ H + 60(30)	CO ₂ H 3a 20(5) CO ₂ H	20	80(35)	25(14) ^a	85(80)
1a	<i>p</i> -xylene:MeCN:H ₂ O = 5:3:2 (pH=4.5)	2a + 32(30)	3a 65(15)	20	97(45)	67(33) ^a	97(85)
1a	<i>p</i> -xylene:MeCN:H ₂ O = 5:3:2 (pH=4.5) 5 mol% BHT ^b	2a + 45	3a 5	20	50	10 ^a	92
1a	<i>p</i> -xylene:MeCN:H ₂ O =1:3:2 (pH=4.5)	2a + 2	3a 96	26	98	98 ^a	98
	H 1 M in MeCN:H ₂ O (2 a (pH= 4.5)	2:1)	CO ₂ H	8 5)	95(15)	99(99) ^a	99(99)
	H 1 M in MeCN:H ₂ O (2 (pH= 4.5) 2 a'	2:1)	CO ₂ H 98(9) CO ₂ H	5 7)	98(97)	99(99)	99(99)
	1b :MeCN:H ₂ O = 5:3:2 (pH=4.5)	CO ₂ H + 2b 50(30)	CO ₂ H CO 3b 45(5)	2 ^H 20	95(35)	47(14)	95(85)
	1c:MeCN:H ₂ O = 5:3:2 (pH=4.5)	CO ₂ H + 2c 42(30)	CO ₂ H 3c 53(10)	20 ₂ H	96(40)	55(25)	96(85)

a. p-Toluic acid and 4-CBA are intermediates and can be further converted to terephthalic acid. The only final product observed is terephthalic acid. Therefore, the true selectivity should be ~100% for all processes. b. BHT= butylated hydroxytoluene, a known inhibitor for peroxidation chain reactions.

germinal diol, which is commonly known to be unstable and will rapidly undergo dehydration to form *p*-methylbenzaldehyde (Fig. 2(a))²⁷, which can be easily oxidized and converted to carboxylic acid functionality upon exposure to ozone in the dark. Note that the bond strengths of benzylic C-H, aromatic C-H, and O-H bonds are ~90, ~110, and ~105 kcal/mol, respectively²⁸. Direct insertion of singlet O(¹D) atom to the weakest benzylic C-H bond requires cleavage of one benzylic C-H bond and formation of two bonds (i.e., the C-O and O-H bonds), which is exothermic and thermodynamically allowed/favored.

In the case of *p*-xylene-acetonitrile-water system, the reaction mechanism is likely to be different from the above neat *p*-xylene system, since both ozone and singlet $O(^{1}D)$ are known to react with water molecule to generate hydroxyl radical (see, equations (3) & (4) in Fig. 2(b))^{29,30}. The formation of hydroxyl radical was confirmed by EPR measurements (Fig. S5). Hydroxyl radical is known to be able to abstract a hydrogen atom from saturated hydrocarbons and initiate a peroxidation chain reaction, in the presence of molecular oxygen, to generate hydroperoxides³¹. In literature, it was reported that hydroxyl radical can abstract a benzylic hydrogen atom from

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aqueous p-xylene with a rate constant³² of ~8.4 x 10^8 M⁻¹s⁻¹. The H atom abstraction rate of hydroxyl radicals was shown to become much slower in dipolar or aprotic solvent environment³¹. In the current p-xylene-acetonitrile-water system, a similar selective Hatom abstraction at the benzylic position might occur to generate pmethylbenzyl radical. Note that the benzylic C-H bond strength (~90 kcal/mol) is much weaker than the aromatic C-H bond (~110 kcal/mol) (Fig. 2(b)), which favors selective H-atom abstraction by hydroxyl radical from the benzylic position. The formation of pmethylbenzyl radical was detected and confirmed by EPR measurements (see, supplementary Fig. S6). The reaction of benzyl radicals with molecular oxygen results in the formation of benzylperoxyl radical, which can also abstract hydrogen atom from another p-xylene molecule to form p- methylbenzyl hydroperoxide and re-generate p-methylbenzyl radical (see equation (5) in Fig. 2(b)). In this peroxidation chain reaction, it involves the formation of one O-H bond (releasing ~105 kcal/mol bond energy) to form pmethylbenzyl hydroperoxide and cleavage of a benzylic C-H bond (absorbing ~90 kcal/mol bond energy) to form p-methylbenzyl radical, which is also exothermic and thermodynamically favored. p-Methylbenzyl hydroperoxide is not stable, especially in the presence of trace amounts of metal ions, and will decompose to generate *p*-methylbenzaldehyde. The of pformation methylbenzaldehyde was reported and detected in the gas phase reaction of *p*-xylene with hydroxyl radical³³. The *p*methylbenzaldehyde can be easily oxidized by ozone to generate ptoluic acid. A similar reaction scheme might occur to convert the methyl group of p-toluic acid and generate dicarboxylic acid product, i.e., terephthalic acid (see, equation (6) in Fig. 2(b)). The existence of the hydroxyl radical-initiated peroxidation chain reaction is supported by the observation that addition of an inhibitor of peroxidation chain reaction, i.e., butvlated hydroxytoluene (BHT)³⁴, dramatically suppresses the yield of TA In the industrial high temperature air oxidation (Table 1). processes, it is commonly observed that the formation of the first electron-withdrawing carboxylic acid functionality decreases the electron density of the para-methyl group, strongly suppresses the reactivity of the para-methyl group in p-toluic acid, and thus hinders further

Table 2. Substrates scope of oxidative C-H functionalization of monosubstituted benzenes. The reactions were carried out either under irradiation using a 100 W Hg lamp (200 mW/cm² at 310 nm) reported first below or in the dark (reported below in parentheses) at room temperature.



(a) neat p-xylene + O₃ + UV







(b) p-xylene-CH₃CN-H₂O + O₃ + UV

 $O_3 + H_2O \longrightarrow 2^{\circ}OH + O_2$ $O(^{1}D) + H_2O \longrightarrow 2^{\circ}OH$



Figure 2. Plausible reaction mechanisms. (a) Neat p-xylene, and (b) p-xylene-CH₃CN-H₂O with ozone upon UV light irradiation.

oxidative conversion of *p*-toluic acid (by molecular oxygen) to terephthalic acid³⁵. Such a phenomenon is well understood, since a benzylic C-H bond with lower electron density will disfavor an oxidation process by oxidants, such as O_2 , metal oxides with poor electron densities. To overcome such a problem, esterification of the *p*-toluic acid to reduce electron withdrawing ability was performed by addition of methanol to the high temperature

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(4)

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Therefore, terephthalate dimethyl ester, instead of reactor. terephthalic acid, was obtained at the end. Alternatively, a higher reaction temperature was adopted to promote the air oxidation of the second methyl moiety in *p*-toluic acid, which is at the expense of more energy consumption, decarboxylation/burning loss of solvent/products, environmental pollution, and production cost. In the current system, the problem of difficulty in the oxidation of the second methyl group in p-toluic acid does not exist at all, since the formation of the first electron-withdrawing carboxylic acid group, in fact, weakens the para-methyl C-H bonds and thus favors/promotes direct benzylic C-H bond insertion by singlet O(1D) and H-atom abstraction by hydroxyl radicals, which is key or the rate determining step in the current O₃-UV irradiation process. In other words, the current process does not rely on direct "oxidation" of benzylic C-H bond by oxidants, and therefore the reaction was not disfavoured/suppressed by the formation of the first electronwithdrawing benzoic acid functionality. Experimentally, p-toluic acid and 4-CBA in the solution can be oxidized and nearly quantitatively converted to PTA at room temperature (Table 1). When the carboxylic acid group is located at ortho- or meta- position, the electron-withdrawing (or benzylic C-H bond weakening) effect on the methyl group becomes less effective, leading to slightly lower yields of dicarboxylic acid products than the para isomer under the same condition (Table 1). The co-precipitation of large amount ptoluic acid (as well as some 4-CBA) in the final crude solid precipitates is most probably due to poor solubility of polar *p*-toluic acid and 4-CBA in non-polar p-xylene. Addition of acetonitrilewater co-solvent to *p*-xylene can help dissolve and keep *p*-toluic acid and 4-CBA intermediates in the solution phase, allowing easier access by oxidants and further oxidative conversion of, otherwise, insoluble p-toluic acid and 4-CBA solid to PTA. Experimentally, we did not observe (by ¹H NMR) any products deriving from hydroxyl radical attack at the benzene ring of p-xylene, which is most probably due to the much less stability of the ring-opened hexadiene-OH adducts, as compared to the *p*-methylbenzyl radical generated via hydrogen atom abstraction at the benzylic position. In addition, much weaker benzylic C-H bond than the aromatic C-H bond also favors selective H atom abstraction by hydroxyl radical at the benzylic position. In the literature, it was reported that the ozone consumption rate in aqueous p-xylene solution is 70 fold larger than that in aqueous benzene, suggesting that attack of hydroxyl radical at the benzylic protons is the major/dominant process over that at the benzene ring moiety³⁶.

In the literature, it was ever reported that ozone was used as an additional oxidant, besides oxygen/air, in the oxidative conversion of p-xylene to terephthalic acid.³⁷⁻⁴⁰. The common features of these earlier work are that transition metal catalysts, high temperature (90~100 °C), and corrosive acetic acid and bromides have to be used in the reaction. The main function of ozone there was to shorten the induction period of time for onset oxidation of p-xylene and to lower down the reaction temperature a little bit, from 150 to 90 °C. The conversion of p-xylene to TA mainly relies on the transition metal catalysts. In the absence of transition metal

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catalysts, no TA was obtained by using ozone alone³⁷_{Arlee} other words, transition metal catalysts are absolutely headed in these three papers for the oxidative conversion of p-xylene to TA. Overall, these earlier work did not resolve the above-mentioned key problems involved in the current industrial production of TA. In the current work, we use a combination of ozone treatment and UV irradiation at room temperature/ 1 atm atmosphere to oxidatively convert pX to TA without the need of any transition metal catalysts, minimized production of global warming gas, ozone depleting gas and wastewater, as well as less high energy consumption. Large parts of the problems involved in the current industrial AMOCO-MC processes are resolved.

It was reported in the literature that ozone and hydroxyl radical were potent oxidants for the removal of organic pollutants in both the atmosphere and polluted water^{41,42}. Both ozone and hydroxyl radical-mediated oxidation reactions were never adopted to synthesize useful organic compounds in organic solutions. The current process is very simple, green and sustainable with low energy consumption, and has great potential to replace the harsh industrial processes (Co2+, Mn2+, bromide, acetic acid, 200 °C, air, 15~30 atom, and hydropurification of 4-CBA at >270 °C, H_2 >70 atm. on Pd/C catalyst) for the synthesis of o-/m-/p-phthalic acids, benzoic acid, acetophenone and benzophenone. From the Green Chemistry Metric point of view, the current process has an E factor of ~0.118, which is substantially smaller than the value of 3.14~10.14 for the industrial AMOCO-MC process (Table 3, and also the section of "Green Chemistry Metric Evaluation" section in the supplementary information for details of calculations). Besides the Green Chemistry Metric values, the energy consumption of the current process is also another important factor to be considered when comparing to the industrial AMOCO-MC process. To avoid distraction of the main focus of the current new chemical process, we leave the detail energy and cost analysis of terephthalic acid production from the current new process to a future manuscript.

Table 3. Side-by-side comparison of Green Chemistry Metric valuesfor the industrial AMOCO process and the current work.

No	Green metrics values	Industrial process	Current process
1	E-factor	3.14~10.14	0.118
2	Atom economy	82%	82%
3	Carbon efficiency	90.2%	92.2%
4	Reactiion mass efficiency	74.1%	75.6%
5	Selectivity of terephthalic aci	d 95%	98%

Conclusions

We have presented an unprecedented low energy demanding green process to resolve problems associated with metal bromide catalysts-based industrial process, and to oxidatively convert pX to TA at an exceptionally mild condition of room temperature and 1

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atmosphere by ozone treatment and concurrent UV irradiation of pX. Experimental results clearly demonstrate that singlet $O(^{1}D)$ atom and hydroxyl radical-mediated oxidation preferentially occurs at the benzylic C-H bonds over the aromatic C=C and C-H bonds in pX. We have also developed a simple solvent washing process for purification of crude TA, which prevents the necessity of the high energy demanding industrial "hydropurification" process and consequently prevention of producing huge amount of wastewater. The current method is greener and more sustainable than the current industrial process for production of pTA (E factor 0.118 vs. 3.14-10.14), has great potential to replace the industrial pTA production processes to prevent generation/release of several hundred million tons of wastewater/ global warming gas (CO2)/ ozone-depleting gas (CH₃Br) per year, reduces substantially the energy consumption, as well as avoids environmental air/soil pollution to the only earth we have.

Experimental

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General procedure for oxidative C-H functionalization of p-xylene.: A dry pressure tube of 20 mL capacity was charged with p-xylene (5 mL) and 5 mL of CH_3CN-H_2O (3:2 v/v, pH= 4-4.5). The pressure tube was equipped with a Teflon septum and a magnetic stirrer bar. Ozone-containing gas (~10% O₃ in O₂ gas) was bubbled into the pxylene-CH₃CN-H₂O solution and simultaneously irradiated by a 100 W Hg lamp (200 mW/cm² at 310 nm) for 20 h at room temperature. Ozone was generated from an ozone generator (C-labsky series, model no. c-I010-DT) using pure oxygen gas as the oxygen source. The oxygen gas flow rate is 0.45 mL/min, which is equivalent to an ozone production rate of 1.56×10^{-5} mole/h. A Teflon tube was used to transport the ozone-containing gas flow to the reactor. The reactor was connected to a chilled water-methanol circulator (-5 to -10 °C) condenser (to trap evaporating reactants and intermediates, and to maintain high mass balance). For substrates having higher freezing points, the temperature of the condenser was set between 5~10 °C. During irradiation, a white solid was slowly formed and The crude solid products were collected by precipitated. centrifugation, and re-dissolved in CDCl₃, DMSO or CDCl₃-DMSO mixture for ¹H NMR (at 600 MHz) and ¹³C NMR (at 150 MHz) measurements. Data reported as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad. All starting materials were commercially available and used as received without further purification

For other details of experimental procedures, please refer to the supplementary materials.

Supporting Information is available in the online version of the paper. This material is available free of charge from the corresponding author upon request. Correspondence and requests for materials should be addressed to KCH.

Conflicts of interest

There are no conflicts of interest to declare.

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Notes and references

- 1 G.A. Kraus, G.R. Pollock III, C.L. Beck, K. Palmera, and A.H. Winter, *RSC Adv.* 2013, **3**, 12721.
- 2 R.A. Sheldon, *Green Chem.* 2014, **16**, 950.
- 3 Purified Terephthalic Acid (PTA) Properties, Production, Price, and Market, Plastics Insight 2019 at <u>https://www.plasticsinsight.com/resin-intelligence/resin-prices/purified-terephthalic-acid-pta/.</u>
- 4 R.A.F. Tomas, J.C.M. Bordado, and J.F.P. Gomes, *Chem. Rev.* 2013, **113**, 7241.
- 5 E.A. Karakhanov, A.L. Maksimova, A.V. Zolotukhinaa, and V.A. Vinokurov, *Russian J. Appl. Chem.* 2018, **91**, 707.
- 6 E. Pérez, J. Fraga-Dubreuil, E. García-Verdugo, P.A. Hamley, W.B. Thomas, D. Housley, W. Partenheimer and M. Poliakoff,
 - Green Chem. 2011, **13**, 2389.
- 7 J.B. Dunn, and P.E. Savage, *Green Chem*. 2003, **5**, 649.
- 8 R. Kleerebezem, J. Beckers, L.W.H. Pol, and G. Lettinga, *Biotech. Bioeng.* 2005, **91**, 169.
- 9 H. Kopnick, M. Schmidt, W. Brugging, J. Ruter, and W. Kaminsky, Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH Verlag, Weinheim, 1992.
- 10 A. Azarpour, and G. Zahedi, Chem. Eng. J. 2012, 209, 180.
- 11 R. Pellegrinia, G. Agostini, E. Groppo, A. Piovano, G. Leofantia, and C. Lamberti, *Journal of Catalysis* 2011, **280**, 150.
- N. Pernicone, M. Cerboni, G. Prelazzi, F. Pinna, and G. Fagherazzi, Catalysis. Today 1998, 44, 129.
- 13 M. Li, T. Ruddy, D. Fahey, D.H. Busch, and B. Subramaniam, *ACS Sustainable Chem. Eng.* 2014, **2**, 823.
- 14 X. Zuo, F. Niu, K. Snavely, B. Subramaniam, and D.H. Busch, *Green Chem.* 2010, **12**, 260.
- 15 Z.W. Luo, and S.Y. Lee, *Nature Comm.* 2017, **8**:15689.
- 16 J. Pang, M. Zheng, R. Sun, A. Wang, X. Wang, and T. Zhang. Green Chem. 2016, 18, 342.
- 17 J.J. Lee, and G.A. Kraus, Green Chem. 2014, 16, 2111.
- 18 K.C. Hwang, and A. Sagadevan, Science 2014, 346, 1495.
- 19 L.Y. Hong, T.L. Zhang, J.G. Zhang, J.Y. Guo, K.B. Yu, *Molecules* 2005, **10**, 978.
- 20 M.S. Chen, and M.C. White, Science 2007, 318, 783.
- 21 T.Y. Newhouse, and P.S. Baran, Angew. Chem. Int. Ed. 2011, 50, 3362.
- 22 K. Chen, A. Eschenmoser, and P.S. Baran, *Angew. Chem. Int. Ed.* 2009, **48**, 9705; and cited references therein.
- 23 Y. Matsumi, F. J. Comes, G. Hancock, A. Hofzumahaus, A. J. Hynes, M. Kawasaki, and A. R. Ravishankara, *J. Geophys. Res.* 2002, **107 (D3)**, 4024.
- 24 Y. Matsumi, and M. Kawasaki, Chem. Rev. 2003, 103, 4767.
- 25 P. Michaudl, and R. J. Cvetanovic, J. Phys. Chem. 1972, **76**, 1375.
- 26 T.H. Varkony, S. Pass, and Y. Mazur, J. C. S. Chem. Comm. 1975, **1975**, 457.
- 27 I. Ignatyev, M. Montejo, P.G.R. Ortega, and J.J.L. Gonzalez, Phys. Chem. Chem. Phys. 2011, 13, 18507.
- 28 S.J. Blanksby, and G.B. Ellison, Acc. Chem. Res. 2003, 36, 255.
- 29 E. Reisz, W. Schmidt, H.P. Schuchmann, and C. Von Sonntag, *Environ. Sci. Technol.* 2003, **37**, 1941.
- 30 B.J. Finlayson-Pitts, and J.N. Pitts Jr., *Science* 1997, **276**, 1045.

6 | J. Name., 2012, 00, 1-3

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- Journal Name
- 31 S. Mitroka, S. Zimmeck, D. Troya, and J.M. Tanko, J. Am. Chem. Soc. 2010, 132, 2907.
- 32 K. Sehested, H. Corfltzen, H.C. Christensen, and E.J. Hart, J. Phys. Chem. 1975, 79, 310.
- 33 Z. Fan, P. Lioy, C. Weschler, N. Fiedler, H. Kipen, and J. Zhang Environ. Sci. Technol. 2003, **37**, 1811.
- 34 G. W. Burton, and K. U. Ingold, J. Am. Chem. Soc. 1981, 103, 6472.
- 35 Y. Xiao, W. P. Luo, X. Y. Zhang, C. C. Guo, Q. Liu, G. F. Jiang, and Q. H. Li, *Catal. Lett.* 2010, **134**, 155.
- 36 J. Hoigne, and H. Bader, H. *Water Res.* 1983, 17, 173.
 37 G.A. Galstyan, V.A. Yakobi, and M.M. Dvortsevoi, *Petroleum Chem. USSR* 1976, 16, 465.
- 38 H. Pan, et al. Science Asia 2018, 44, 212.
- 39 T. Takaya, T. Koga, and T. Hara, Bulletin of the Chemical Society of Japan 1965, 39, 654.
- 40 M. Waser, W.G. Jary, P. Pöchlauer, and H. Falk, J. Molecular Catalysis A: Chemical 2005, 236(1-2), 187.
- 41 U. von Gunten, Water Research 2003, 37, 1443.
- 42 R. Atkinson, and J. Arey, Chem. Rev. 2003, 103, 4605.

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p-Xylene was oxidatively converted to terephthalic acid at room temperature with ~98% selectivity in the absence of any catalysts via ozone treatment with concurrent UV irradiation without productions of global warming gases.

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