Metal–Catalyzed, Photo-Assisted Selective Transformation of Tertiary Alkylbenzenes and Polystyrenes into Carbonyl Compounds

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Every year, thousands of tons of polystyrene are produced and discarded, filling landfills and polluting the marine environment. Although several degradation alternatives have been proposed, the need for an effective procedure for the chemical recycling of polystyrene still remains. Here, a vanadium-catalyzed reaction, assisted by visible light, promoted the direct, selective conversion of tertiary alkylbenzenes into acetophenone and other ketone derivatives. Likewise, standard polystyrene samples as well as polystyrenes from insulation and packaging waste could be chemically recycled into acetophenone in a scalable way regardless of their molecular weight, polydispersity, or form. Preliminary mechanistic investigations revealed the participation of singlet oxygen, superoxide, and hydroxyl radical species in this homogenously catalyzed process. Acetophenone could be used as an additive to accelerate the reaction and to increase the yields in some cases.

Introduction

Polystyrene (PS) is one the most widely used plastics for transportation composites, food packaging, thermal insulation in construction, appliances, and medical products, thus occupying about 6–7% of the total market share.[1] On average, 10 million tonnes of polystyrene were produced globally in 2018,[2] and considering the relatively short lifespan of many PS products [e.g., food and hot drinks packaging made of expanded PS (EPS)] and their poor recycling rate, PS waste has become a serious global environmental concern, with an increasingly higher percentage of PS in land and marine debris.[1,3] Promising research on PS degradation and recycling (e.g., chemical depolymerization and pyrolysis,[4] photolysis and mineralization,[5] mechanochemical treatment,[6] and biodegradation[7]) has been published. However, in contrast with other commonly used plastics, much progress is still needed to obtain high yields and selectivities for valuable raw materials other than styrene.[8]

Following our research on the oxidation of organic compounds by molecular oxygen,[9] we envisaged that under a strongly oxidizing, aerobic environment PS should undergo a selective cleavage at the benzylic C—C bond to provide a valuable carbonyl or carboxy compound. This presented itself as a formidable challenge considering the scarcity of reports on the selective preparation of carbonyl compounds by oxidative cleavage even of simple tertiary alkyl aromatic hydrocarbons using molecular oxygen as the sole oxidant. Indeed, although stronger oxidizing agents such as ozone,[10] iodosobenzene,[11] and several peroxides and persulfates[12] provided acetophenone from tertiary alkyl benzenes with relative success, low selectivities towards the latter ketone have been observed in exclusively aerobic processes (mixtures of the corresponding α,α-dialkylbenzyl hydroperoxide, dialkylbenzyl alcohol, and acetophenone are generally obtained).[13] Only in a few cases, acceptable conversion rates and selectivities towards the carbonyl compound have been reported, at the cost of relatively high pressures, and substrate scopes are usually limited to cumene and 1,1-diarylalkanes.[14]

Acetophenone is a valuable raw material for the production of copolymer resins, perfumes and fragrances, and a precursor of biologically active compounds.[15] This colorless liquid with a floral odor can be isolated from several plants and fruits, although because of its great demand, bulk production from fossil sources is required. In addition to classical methods such as Friedel–Crafts acylation of benzene and Wacker-type oxidation of styrene, acetophenone is also produced on an industrial scale as a by-product in the commercial production of propylene oxide mediated by ethylbenzene. Interestingly, reduction of acetophenone to phenylethanol followed by dehydration is used to prepare styrene.[16]

A selective, high-yielding conversion of tertiary alkylbenzene derivatives, and in particular, of PS into acetophenone is therefore highly desirable. With this aim in mind, we started a research program that focused on the use of oxygen at atmospheric pressure as the only oxidant for the above transformation.[17] Free radical chain reactions, common in autoxidation processes,[18] had to be avoided or at least minimized in order to achieve target selectivity in this particularly challenging C—C bond breaking procedure.

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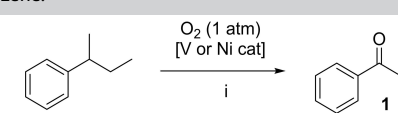European Chemical
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Results and Discussion

Taking *sec*-butylbenzene as model substrate, an initial screening of reaction conditions combining different metal sources, ligands, solvents, and additives was conducted. From the very beginning, it became clear that only reactions carried out in a polyol solvent [ethylene glycol, glycerol, polyethylene glycol (PEG)] produced acceptable conversions ($>10\%$). Something similar occurred with metal catalysts. Indeed, from all the metal sources assayed, acetophenone was preferentially obtained only with Ni and V catalysts (Supporting Information, Table S1). Several P- and N-ligands were discarded due to the low yields obtained, and PEG-200, PEG-1500, ethylene glycol, and glycerol solvents for the same reason and the problematic and laborious work-up and purification steps required. Low conversions were observed in PEG-1500, and although direct column chromatography of the reaction crude provided best results for reactions carried out in PEG-400, this direct purification protocol failed for ethylene glycol and glycerol. A similar behavior was observed after addition of water to the crude and extraction with diethyl ether, ethyl acetate, or dichloromethane. After this initial screening, a further optimization of reaction variables (Table 1) involved the selection of the most suitable metal source [VO(acac)$_2$], 1,2,4-triazole ligands MBTB (methyl 3,5-bis((1*H*-1,2,4-triazol-1-yl)methyl)benzoate) and B1T (1-benzyl-1*H*-1,2,4-triazole), and NaOAc as base (Table 1, entry 14).

Once the optimal temperature and reaction time under these thermal conditions were defined (Figure 1a), and considering the substantial number of previous reports on light-induced non-selective degradation of polystyrenes[19] and photoinduced oxidation of alkylbenzene derivatives leading to low yields or main products other than acetophenone,[20] we carried out similar experiments in which the reaction was irradiated with a white LED lamp (10 W, $\lambda = 400$–800 nm). To our delight, the reaction time was shortened from 96 to 24 h with a similar yield and complete selectivity (Figure 1a). Accordingly, the reaction yield of the target oxidative cleavage was evaluated as a function of the visible light wavelength. As shown in Figure 1b, the best results for the four effective catalyst systems were obtained by irradiation with light of 400–440 nm. Table 2 shows the experiments performed to reduce the catalyst loading and some blank experiments in order to verify the need for both V source and ligands (Table 2,

Table 1. Selected optimization experiments for the aerobic cleavage of *sec*-butylbenzene.[a]

Entry	Conditions[b]	PhAc yield[c] [%]	Conv. [%]
1	NiCl$_2$, Htrz, K$_2$CO$_3$	7	20
2	[Ph$_2$P(CH$_2$)$_3$PPh$_2$]NiCl$_2$, B1T, KOtBu	10	25
3	Ni(PPh$_3$)$_2$Cl$_2$, MBTB, NaOAc	11	28
4	NiBr$_2$, imidazole, NaOAc	6	14
5	Ni(OAc)$_2$, B1T, NaOAc	17	32
6	NiBr$_2$, B1T, NaOAc	23	39
7	Ni(NO$_3$)$_2$, Htrz, Et$_3$N	19	36
8	NiBr$_2$, MBTB, NaOAc	22	40
9	V$_2$O$_5$, imidazole, Et$_3$N	9	21
10	V$_2$O$_5$, Htrz, NaOAc	22	42
11	V$_2$O$_5$, MBTB, NaOAc	31	52
12	VCl$_3$, Htrz, KOtBu	17	39
13	VCl$_3$, B1T, NaOAc	39	42
14	VO(acac)$_2$, B1T, NaOAc	59	89
15	VO(acac)$_2$, Htrz, Et$_3$N	26	43

[a] Reaction conditions: *sec*-butylbenzene (1 mmol), O$_2$ (1 atm), Ni or V source (10^{-2} mol%), ligand (10^{-2} mol%), base (0.1 mmol), PEG-400 (1 mL), 120 °C, 96 h. [b] MBTB: methyl-3,5-bis((1*H*-1,2,4-triazol-1-yl)methyl)benzoate; B1T: 1-benzyl-1*H*-1,2,4-triazole; Htrz: 1*H*-1,2,4-triazole. [c] Isolated yields.
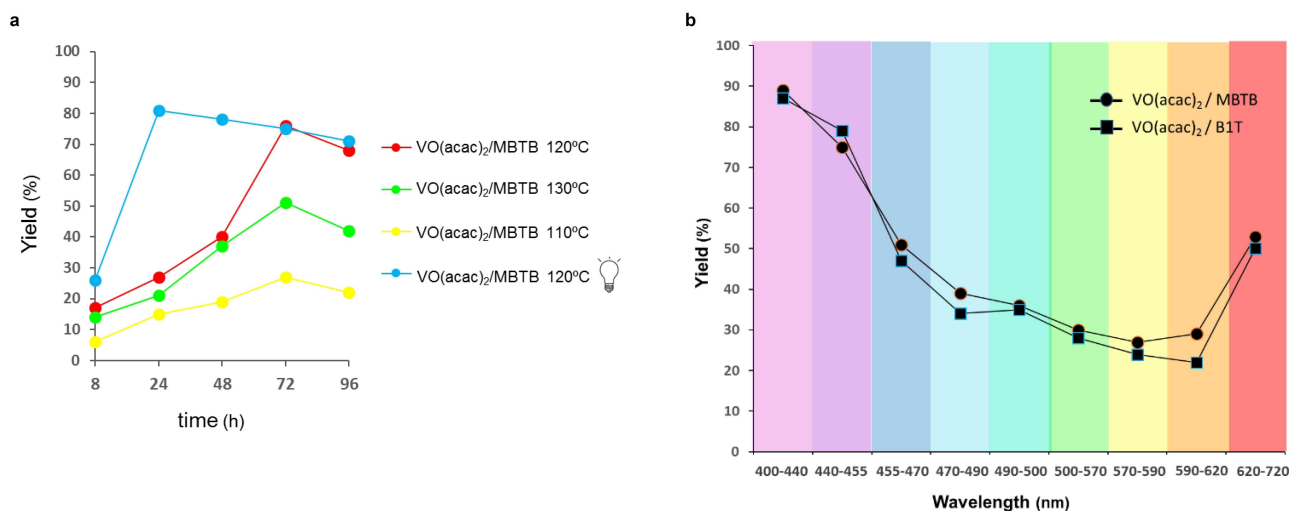

Figure 1. The role of visible light in optimization assays. (a) Optimization of temperature and reaction time for the metal-catalyzed cleavage of *sec*-butylbenzene. The process is clearly accelerated by irradiation of visible light. Reaction conditions: *sec*-butylbenzene (1 mmol), O$_2$ (1 atm), VO(acac)$_2$ (10^{-2} mol%), MBTB (10^{-2} mol%), NaOAc (0.1 mmol), PEG-400 (1 mL). Isolated yields. (b) Effect of wavelength on metal-catalyzed cleavage of *sec*-butylbenzene. Reaction conditions: *sec*-butylbenzene (1 mmol), O$_2$ (1 atm), VO(acac)$_2$ (10^{-2} mol%), MBTB or B1T (10^{-2} mol%), NaOAc (0.1 mmol), PEG-400 (1 mL), hν, 24 h. Isolated yields.

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Table 2. Adjustment of catalyst loading and control experiments.[a]

Entry	Loading [mol%]	VO(acac)$_2$/MBTB		VO(acac)$_2$/B1T	
		Yield[b] [%]	Conv. [%]	Yield[b] [%]	Conv. [%]
1	0.01	86	100	83	100
2	0.001	85	100	81	100
3[c]	0.0001	77	100	80	100
4[c]	0.00001	15	75	20	84
5[d]	0.01	–	<5	–	<5
6[e]	0.01	34	48	34	46
7[f]	0.01	62	66	57	60

[a] Reaction conditions: sec-butylbenzene (1 mmol), O$_2$ (1 atm), VO(acac)$_2$, MBTB or B1T, NaOAc (0.1 mmol), PEG-400 (1 mL), 120 °C, 24 h, hν (400–440 nm). [b] Isolated yield of acetophenone. [c] Reaction time: 48 h. [d] Control experiment in the absence of any V source. [e] Control experiment in the absence of ligand. [f] Control experiment in the absence of base.

entries 5–7). Accordingly, the reaction conditions displayed in Table 2, entry 2 were selected as the optimal ones.

As shown in Table 3, a number of structurally diverse tertiary alkylbenzene derivatives were then reacted under the optimized conditions. In addition to sec-butylbenzene, its homologue sec-pentylbenzene as well as cumene provided acetophenone with good yields. Other functionalized alkylarenes, such as 2-phenylpropanal, 2-phenylpropanoic acid, (S)-2-(4-isobutylphenyl)propanoic acid (commonly known as ibuprofen), and sodium (S)-2-(6-methoxynaphthalen-2-yl)propanoate (naproxen sodium), were also submitted to this molecular oxygen-mediated reaction furnishing selectively the corresponding aryl methyl ketones. Finally, benzophenone was satisfactorily isolated from two diaryl- and triarylalkane derivatives, namely diphenylacetic acid and triphenylmethane. Both vanadium alternative catalyst systems provided similar results. Depending on the substrate and the catalyst system employed, it was necessary to prolong the reaction time.

Subsequently we applied the procedure to PS, adjusting the amount of PEG-400 so that the reaction could be carried out in solution, as with previous tertiary alkylarenes. Indeed, 1 mL of PEG-400 per mmol of PS implied very little volume of the polyol compared to the mass of PS (<1 μL on a 100–200 mg scale), and no reaction took place in this case. After several experiments using commercially available PS1 (M_W = 35000, M_w/M_n = 1.09) as model substrate, an optimal weight of polystyrene/weight of VO(acac)$_2$/volume of PEG ratio ($w_{PS}/w_{VO(acac)_2}/v_{PEG}$) of 150 mg:5 mg:100 μL was found (Supporting Information, Table S2).

The scope of this reaction was evaluated with various PS standards, each with relatively low molecular weights (PS1–PS5), the results of which are displayed in Table 4. Positive results were obtained regardless of the M_W of the polymer. Two samples of expanded PS (PS6 and PS7) of considerably higher molecular weight were collected from waste packaging, analyzed, and submitted to the same reaction conditions to provide acetophenone with good yields. A similar behavior was observed for a sample of extruded PS taken from waste insulation material (PS8), which, like PS6 and PS7, had a considerably higher degree of polydispersity. Finally, even

better results were obtained from a sample of a crystal PS collected from a broken CD case (PS9). Accordingly, it can be concluded that the outcome of the reaction depends on neither the average molecular weight of the polymer nor the forms produced (injection-molded, vacuum-formed, extruded, expanded) nor polydispersity. Regarding reaction time, although reactions from PS1 and PS2 took place within 24 h, heating was continued for 24 h in order to produce optimal results from PS3–PS9.

Another important research issue was the evaluation of the scalability of the procedure. In this regard, 20 g of PS1 was reacted under the optimized conditions [VO(acac)$_2$/MBTB], providing acetophenone with a yield of 66%. A sequence of depolymerization of polystyrene followed by hydration of styrene monomer and oxidation of resulting 1-phenylethanol would also provide acetophenone, but at the cost of a two/three-step-sequence. Moreover, depolymerization of polystyrene leading to styrene monomers is a process that often involves heating to 350–400 °C and even higher temperatures to give mixtures of monomers and oligomers at best.[4e–m]

Although a variety of polystyrenes were selectively degraded to acetophenone, this procedure failed to provide the target ketone when divinylbenzene-cross-linked polystyrenes and poly(acrylonitrile-co-butadiene-co-styrene) or poly(styrene-co-acrylonitrile) were subjected to the same reaction conditions. In fact, very low conversions (<5%) were observed in all cases.

A number of experiments were then carried out with a view to understanding the reaction mechanism. sec-Butylbenzene and other simple alkylbenzenes were the substrates selected for these experiments on the basis of the simplicity of work-up, vanadium catalyst/product separation, or detection of chemical entities. Similar results were observed when related assays were performed on PS samples.

Labelling experiments using a mixture of $^{16}O_2$ and $^{18}O_2$ at atmospheric pressure were combined with shorter reaction times with the aim of detecting reaction intermediates as well as finding the source of the oxygen atom in the ketone products. As shown in Figure 2a, ^{18}O-labelled benzophenone was obtained when triphenylmethane was treated with a 1:1 mixture of $^{16}O_2$ and $^{18}O_2$ at atmospheric pressure for 24 h. Interestingly, in addition to the desired product showing a ^{18}O-labelling degree of 51% [as determined by mass spectrometry (MS)], partially labelled phenol and triphenylmethanol were also observed by gas chromatography (GC)-MS.

Although the yield of phenol was lower than that of acetophenone, we assume that this aromatic alcohol is the by-product of the reaction, whereas triphenylmethanol would derive from a reaction intermediate. In this regard, phenol was the only by-product isolated, although traces of acetaldehyde and ethanol were detected from the reaction with sec-butylbenzene.

Almost equivalent kinetic curves (Figure 2b) were plotted for both model substrates (sec-butylbenzene and PS1). The lack of induction period observed in these kinetic studies suggests the participation of a truly homogeneous catalyst.[21] In addition, the acceleration observed as the concentration of target ketone increases suggest some kind of autocatalysis.[22]

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Table 3. Oxidative cleavage of tertiary alkylarene derivatives: substrate scope.[a]

Substrate	Product	VO(acac)$_2$/MBTB Yield[b] [%]	Conv. [%]	VO(acac)$_2$/B1T Yield[b] [%]	Conv. [%]
	1	85	100	81	100
	1	76[c]	94	71[d]	95
	1	80	95	84	100
	1	81	93	82	94
	1	85	100	95	100
	2	81[c]	94	87[c]	100
	3	42	63	45	60
	4	90	100	94	100
	4	76[c]	95	75[c]	93

[a] Reaction conditions: Tertiary alkylarene (1 mmol), O$_2$ (1 atm), VO(acac)$_2$ (10^{-3} mol%), MBTB or B1T (10^{-3} mol%), NaOAc (10^{-1} mmol), PEG-400 (1 mL), 120 °C, 24 h, hν (400–440 nm). [b] Isolated yield. [c] Reaction time: 48 h. [d] Reaction time: 72 h.

A second set of experiments were then targeted at evaluating the participation of excited states and reactive oxygen species, such as singlet oxygen (^{1}O$_2$), superoxide radical anion ($^\bullet$O–O$^-$) or hydroxyl radicals (HO$^\bullet$) in the vanadium-catalyzed processes. A significant acceleration of the reaction rate was observed when adding the photo-Fenton reagent[23] to the reaction mixture at acidic and neutral pH values, thus suggesting that hydroxyl radical and hydrogen peroxide may be involved in the reaction mechanism. This suggestion was confirmed by the complete inhibition of the reaction from PS1 in the presence of *iso*-propanol, a common probe for HO$^\bullet$.[24] No reaction took place in the presence of benzoquinone, a super-oxide radical scavenger frequently used to prove the intermedi-acy of such radical species.[25] Interestingly, addition of catalytic

amounts of NaN$_3$ (5 mol%) also hampered the reaction. Sodium azide is known to be a specific quencher of singlet oxygen.[26] Moreover, 0.02 equiv. of eosin Y, a well-established photo-sensitizer used to produce singlet oxygen from triplet oxygen,[27] significantly accelerated the reaction so that comparable yields [79%, VO(acac)$_2$/B1T] were obtained in just 10 h (Supporting Information, Table S4). As in the previous set of experiments, similar results were obtained from both PS1 and *sec*-butylbenzene.

Several experiments have indicated the involvement of benzyl radicals in the partial or non-selective degradation of PS.[19c–e,20a,28] In our case, a very faint electron paramagnetic resonance (EPR) signal was detected, although it could have been due to the use of PEG-400 as reaction media. However,

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Table 4. Metal-catalyzed photo-assisted transformation of polystyrenes into acetophenone: substrate scope.[a]

PS	PhCOCH$_3$ 1[b] [%] VO(acac)$_2$/ MBTB	VO(acac)$_2$/ B1T	Photo	M_W[c]	M_W/M_n[d]
PS1	85	85		35000	1.09
PS2	58	80		1951	1.183
PS3	89[e]	83[e]		25000	1.06
PS4	58[e,f]	45[e,f]		65000	1.06
PS5	66[e,f]	53[e,f]		5200	1.06
PS6	70[e]	80[e]		211300	1.257
PS7	85[e]	70[e]		353100	1.404
PS8	70[e]	58[e]		269900	1.362
PS9	82[e]	82[e]		430600	1.421

[a] Reaction conditions: PS (150 mg), O$_2$ (1 atm), VO(acac)$_2$ (5 mg, 1.9×10 mmol), MBTB (6 mg, 2.0×10^{-2} mmol) or B1T (6 mg, 3.8×10^{-2} mmol), NaOAc (10^{-1} mol%), PEG-400 (100 µL), 120°C, 24 h, hν (400–440 nm). [b] Isolated yields calculated from the average molecular weight of PS. n values were determined to be 260, 14.5, 186, 484, 39, 1574.5, 2631, 2011, and 3208 for PS1, PS2, PS3, PS4, PS5, PS6, PS7, PS8, and PS9 respectively. [c] M_W: weight-average molecular weight. [d] M_W/M_n: weight-average molecular weight/number-average molecular weight ratio. [e] Reaction time: 48 h. [f] See Figure 2c for further improvements in this reaction.
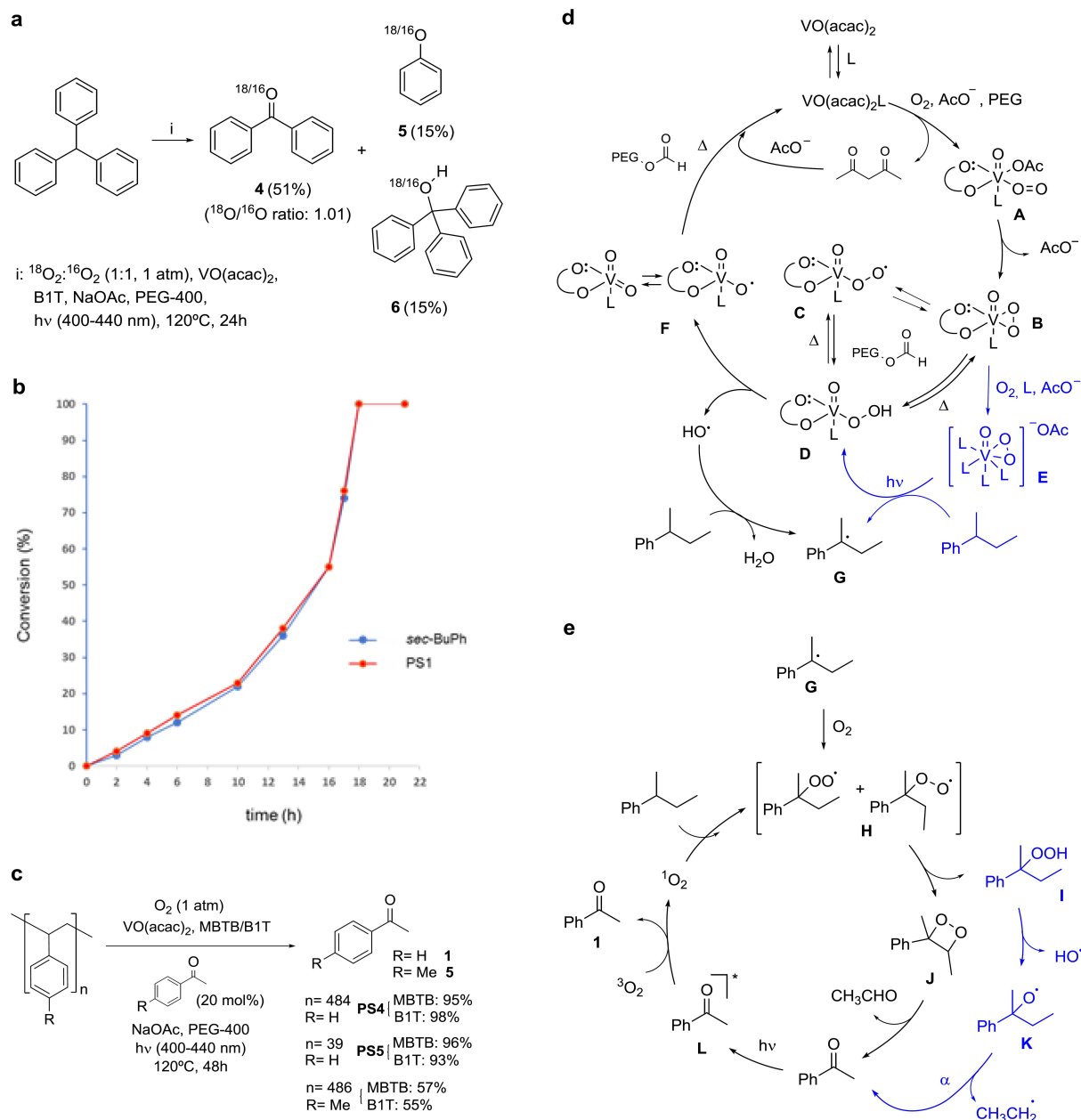
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Figure 2. Mechanistic investigations. (a) ^{18}O Labelling experiments. Isotopic distribution in benzophenone matches with the employed $^{16}O_2/^{18}O_2$ mixture. (b) Conversion rate of *sec*-butylbenzene and PS1 vs. time. Reaction conditions: *sec*-BuPh/PS1 (1 mmol, 150 mg), O_2 (1 atm), VO(acac)$_2$ (10^{-5} mmol, 1.9×10^{-2} mmol), B1T (10^{-5} mmol, 3.8×10^{-2} mmol), NaOAc (10^{-1} mmol), PEG-400 (1 mL), 120 °C, hν (400–440 nm). (c) Effect of addition of catalytic amounts of acetophenone in the chemical recycling of otherwise less reactive PS samples and poly(*p*-methylstyrene). (d) A tentative proposal for the vanadium-catalyzed light-induced formation of benzyl radical (**G**) from *sec*-butylbenzene. (e) Proposed mechanism to explain the selective formation of acetophenone from benzyl radical (**G**). Alternative pathways are disclosed in blue.

1 mol % of 2,2-diphenyl-1-picrylhydrazyl (DPPH) completely inhibited the reaction, and a similar behavior was observed when (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) was added (Supporting Information, Table S4). Both TEMPO and DPPH are conventionally used radical scavengers.[29]

On account of the above experiments and literature reports, we propose the mechanism displayed in Figure 2d to explain the selective formation of ketones **1**–**4** from tertiary alkylbenzene derivatives. After initial coordination of VO(acac)$_2$ with

triazol ligand (MBTB or B1T), oxygen insertion through intermediate **A** would generate vanadium(V) peroxo complex **B**.[30]

Although a radical-based mechanism has been proposed, oxidation of *sec*-butylbenzene could also proceed through interaction with peroxo complexes **B** or **E** in a non-radical (hidden radical) fashion. Indeed, in accordance with the work by Kobayashi and Yamanaka,[31] the aforementioned complexes could promote a direct dissociation of the C—H bond in *sec*-

butylbenzene, and that would explain the faint EPR signal observed. However, the partial degradation of polyethylene glycol under aerobic thermal conditions that generates formate groups (PEGOCOH) should be not ignored.[32] Thermal decomposition of the above formate groups would form transient formyloxyl radical and hydride species.[33] We opted for a redox equilibrium involving participation of the latter reducing species for the formation of superoxide and hydroperoxo complexes **C** and **D**.

Reports on photochemical C–H activation proceeding through transient [O=V–OO•] species generated by irradiation of vanadium oxo–peroxo and *cis*-dioxo complexes have been published, including the aerobic oxidation of dihydroanthracene and other alkylarenes in the presence of [oxo(peroxo)vanadium(V) bis(4,40-*R*-2,20-bipyridyl)] upon light irradiation.[34] In this regard, a supplementary pathway to get benzyl radical **G** would be based on the photoexcitation of oxo(peroxo) V^V complex **E** (alternatively, similar species derived from **B** or **F** could also promote a similar process).

As suggested by Stepovik and Potkina,[35] intracage recombination of the alkylperoxy radical **H** would form dioxetane **J** and hydroperoxide **I**. Decomposition of the former would release acetophenone. Simultaneously, thermal decomposition of alkoxy radical **K**, formed by splitting of hydroperoxide **I**,[20a,36] would also provide acetophenone. A portion of this ketone could turn into photoexcited species **L** upon irradiation, and interaction of the latter with triplet oxygen would generate singlet oxygen, known to activate benzylic C–H bonds,[37] thus generating hydroperoxide **I** again. The fact that singlet oxygen can be generated via direct photo irradiation of molecular oxygen by 765 nm light would account for the otherwise difficult to explain increase in the yield when red light irradiation was used in comparison with green, yellow, and even orange lights (see Figure 1b). Vanadium species **A**–**F**, hydroperoxide **I** and dioxetane **J** were detected by ultra-performance liquid chromatography-electrospray ionization-mass spectrometry (UPLC-ESI-MS) of the reaction crude (Supporting Information).

In their cutting-edge papers of 1976 and 1982, George, Hodgeman, and Geuskens et al. suggested that acetophenone end-groups present in commercially available PS were responsible not only for the yellowing and embrittlement after long-term exposure to sunlight but also for the quicker photodegradation of PS under UV light (310 and 365 nm) leading to complex mixtures. They evaluated the accelerating effect of adding several aromatic ketones such as benzophenone and acetophenone, concluding that these ketones initiated the above photooxidation.[19a,d,30]

Considering the photosensitizing properties of acetophenone, with a quantum yield close to 100%,[31] and its ability to promote hydrogen atom abstraction processes,[32] we decided to add a catalytic amount (20 mol%) of the reaction product, acetophenone, to the starting alkylbenzene and PS1. Unexpectedly, the vanadium-catalyzed process was accelerated considerably, reaching a conversion rate of 80–85% in just 8 h and full conversion in 16 h. In view of these results, we again attempted the transformation of samples PS4 and PS5 into acetophenone with this additive, and after 48 h the reaction yields increased from 45–66 to 93–98% for VO(acac)$_2$/MBTB and VO(acac)$_2$/B1T systems. In addition, this variant was also applied to the reaction from poly(*p*-methylstyrene) ($M_W = 72000$), providing *p*-methylacetophenone **5** with good yields (Figure 2c).

On the basis of generality, scalability and high yields achieved, our protocol can be applied to the tertiary plastic recycling (chemical recycling, defined as "production of basic chemicals or fuels from segregated plastic scrap or plastic material that is part of a municipal waste stream or other source")[33] of polystyrene derivatives.

Conclusion

Acetophenone and other aromatic ketones can be selectively obtained by a controlled aerobic degradation of tertiary alkylbenzenes catalyzed by vanadium catalysts VO(acac)$_2$/MBTB and VO(acac)$_2$/B1T [MBTB: methyl-3,5-bis((1*H*-1,2,4-triazol-1-yl)methyl)benzoate; B1T: 1-benzyl-1*H*-1,2,4-triazole]. This reaction is greatly accelerated by irradiation with visible light (400–420 nm). In addition, acetophenone derivatives are also produced in adequate yields under similar conditions from polystyrenes showing dissimilar average molecular weights, forms, and polydispersity. Molecular oxygen, possibly through singlet oxygen, superoxide radical anion, and hydroxyl radicals, is the source of the ketone oxygen in this homogeneously catalyzed scalable reaction, which can be further accelerated by addition of a catalytic amount of the reaction product acetophenone. This variant allows the selective transformation of otherwise unreactive polystyrene samples and of *p*-methylpolystyrene as well.

Experimental

General procedure for the aerobic cleavage of tertiary alkylbenzene derivatives using the VO(acac)$_2$/MBTB or VO(acac)$_2$/B1T catalyst systems

A round-bottom flask (10 mL) equipped with a magnetic stirrer bar was charged with the tertiary alkylbenzene derivative (1 mmol), NaOAc (8.0 mg, 0.1 mmol), VO(acac)$_2$ (20 μL of a 5×10^{-4} M solution in PEG-400, 10^{-5} mmol), MBTB (20 μL of a 5×10^{-4} M solution in PEG-400, 10^{-5} mmol) or B1T (20 μL of a 5×10^{-4} M solution in PEG-400, 10^{-5} mmol), and PEG 400 (1 mL) at room temperature. The system was purged with molecular oxygen, and an oxygen-filled balloon (1–1.2 atm) was connected. The mixture was irradiated with visible light (400–440 nm) and heated at 120°C under stirring for 24 h. The reaction outcome was monitored by proton nuclear magnetic resonance (^{1}H NMR) spectroscopy. Upon completion, the mixture was cooled to room temperature, and the crude was purified by flash column chromatography using hexane/ethyl acetate ratio as eluent.

General procedure for the selective transformation of polystyrenes into acetophenone using the VO(acac)$_2$/MBTB or VO(acac)$_2$/B1T catalyst systems

A round-bottom flask (10 mL) equipped with a magnetic stirrer bar was charged with polystyrene (150 mg), NaOAc (10^{-1} mol), VO-(acac)$_2$ (5 mg, 1.88×10^{-2} mmol), MBTB (6 mg, 2×10^{-2} mmol) or B1T (6 mg, 3.75×10^{-2} mmol), and PEG 400 (100 μL) at room temperature. The system was purged with molecular oxygen, and an oxygen-filled balloon (1–1.2 atm) was connected. The mixture was irradiated with visible light (400–440 nm) and heated at 120 °C under stirring for 24 h. Upon completion, the mixture was cooled to room temperature, and the crude was purified by flash column chromatography using petrol ether → petrol ether/ethyl acetate (8:2) as eluent.

General procedure for the selective transformation of polystyrene derivatives into aryl methyl ketones using the VO(acac)$_2$/MBTB/aryl methyl ketone or VO(acac)$_2$/B1T/aryl methyl ketone catalyst systems

A round-bottom flask (10 mL) equipped with a magnetic stirrer bar was charged with the polystyrene (150 mg), NaOAc (10^{-1} mol %), VO(acac)$_2$ (5 mg, 1.88×10^{-2} mmol), MBTB (6 mg, 2×10^{-2} mmol) or B1T (6 mg, 2×10^{-2} mmol), aryl methyl ketone (2×10^{-1} mol %), and PEG 400 (100 μL) at room temperature. The system was purged with molecular oxygen, and an oxygen-filled balloon (1–1.2 atm) was connected. The mixture was irradiated with visible light (400–440 nm) and heated at 120 °C under stirring for 24 h. Upon completion, the mixture was cooled to room temperature, and the crude was purified by flash column chromatography using petrol ether → petrol ether/ethyl acetate (9:1) as eluent.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

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