

A sustainable two-phase procedure for V-catalyzed toluene oxidative bromination with H_2O_2 – KBr^\ddagger

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A sustainable V(v) and Mo(vi) catalysed two-phase procedure for bromination of toluene under quite mild conditions is proposed; H_2O_2 is the primary oxidant and KBr is the bromine source; metal precursors are commercially available salts. The reaction is efficient without any additional solvent. By using PhCH_3 as a solvent/substrate good yields, together with interesting selectivity toward the formation of PhCH_2Br , are obtained with both metal ions. Recycling of the catalytic phase is also possible. Useful information on the V-peroxido chemistry was obtained.

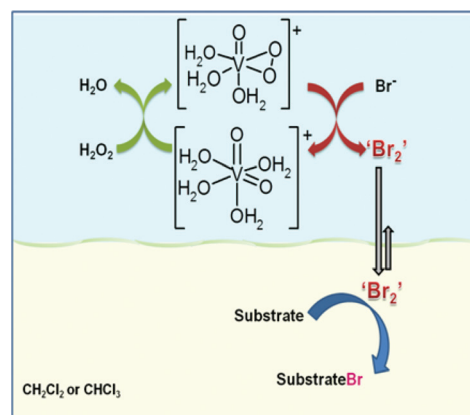
Introduction

Halogen containing organic compounds are primary building blocks in organic synthesis and this is particularly true in the case of bromide derivatives at the benzylic position.¹ Furthermore, these molecules find applications in the field of materials science, pharmaceuticals, agrochemicals and bio-active compounds.²

In a general sense, halogenation is an oxidative process carried out efficiently in nature through enzyme-catalysed reactions where a halide ion is transformed into a halogenating intermediate. Typical examples of these processes are heme-dependent chloroperoxidases, which use H_2O_2 as a primary oxidant and chloride anions to perform electrophilic reactions, and vanadium dependent haloperoxidases, where in the presence of hydrogen peroxide the metal center becomes the active peroxidic species.³

The mode of action of V-dependent bromoperoxidase enzymes (V-BrPO) has stimulated several research groups to search for an effective functional model for their activity.⁴ Our contribution in the field dates back to the 90s last century, when we developed a synthetic procedure for the bromination of organic substrates in a two-phase system (H_2O –chlorinated solvent), Scheme 1.⁵

Our proposal was inspired by the accepted mode of action of V-BrPOs⁴ which, in the presence of H_2O_2 , forms a peroxido-vanadium derivative. This latter, then, oxidizes a bromide ion forming a bromine equivalent intermediate which may either



Scheme 1 Vanadium based two-phase system for oxidative bromination.

brominate an appropriate organic substrate or react with another molecule of a terminal oxidant decomposing it. In spite of the fact that these two reactions occur together, both the chemoselectivity of the enzyme catalysed reactions and the yields of brominated products are very high. This suggests that the formation of the intermediate and the bromination reaction occur in two different compartments of the enzymes. In particular the former process should take place in a hydrophilic portion near the active site of the enzyme, whereas the latter reaction occurs in a hydrophobic region.

Following this line of reasoning, we developed a biphasic procedure (see Scheme 1) where in water a vanadium precursor, H_2O_2 and KBr are dissolved and form a peroxido vanadium derivative which oxidizes Br^- . The brominating intermediate is then transferred into the organic phase, where the functionalization of the substrate takes place.^{5,6} To note, the process in the aqueous phase requires acid conditions, likely to allow protonation of a peroxy oxygen. This system has been accurately studied with aromatic substrates, alkenes and

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†Dedicated to Prof. Maurizio Prato on the occasion of his 60th birthday.

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alkynes and very interesting synthetic results have been obtained.^{5c}

From a sustainable point of view the proposed procedure is interesting because it uses H₂O₂ as a primary oxidant, a cheap source of metal catalysts and safe KBr as a bromine precursor. On the other hand, it suffers from the presence of an organic halogenated solvent. In order to render the system much more appealing, we explored the possibility to perform haloperoxidation of styrene and phenylethyne substituting the organic volatile toxic solvent with a hydrophobic ionic liquid.⁷ Good to excellent yields of brominated products were obtained with styrene and other unsaturated substrates using appropriate imidazolium salts as solvents, much higher than those achieved in the native system.^{5c,7a}

As a logical development, we decided to explore this procedure also for functionalization of toluene at the benzylic position. Bromination in the side chain of aromatic derivatives has been performed with several acid systems containing bromide and an oxidant,^{1,8} eventually in the presence of light.⁸ Also some dibromo disulfonamides have been proposed as effective brominating agents for toluene.⁹ One of the primary problems in all reactions quoted is the competitive formation of dibromo methyl benzene together with bromomethyl benzene. In addition, subsequent hydrolysis of those two bromine containing compounds may produce benzyl alcohol and benzaldehyde respectively, which eventually could be also interesting products, particularly if benzaldehyde is preferentially obtained.

To note, a vanadate–H₂O₂ based bromination reaction, under aqueous conditions, was proposed in 2007 by Hirao.¹⁰ The procedure requires the presence of a surfactant to facilitate the interaction between the insoluble substrates (activated benzenes, double and triple bonds and cyclohexanone) and the catalytic phase. In some cases also in that system a H₂O–chlorinated solvent mixture is required. In another very recent paper hydrogen peroxide and halides were used in the presence of bis[1-methyl-3-(3'-sulfopropyl)imidazolium] hexafluorotitanate to brominate arenes; the main reaction being, under such conditions, the electrophilic attack on the aromatic rings.¹¹

Oxidation of benzylic C–H bonds is an important research topic, recently reviewed.¹² Several papers appeared in the last few years dealing with benzylic oxidation of alkylarenes, using different metal catalysts and primary oxidants.¹³ In particular, benzylic oxidative bromination was performed with a variety of brominating reagents.¹⁴

Our aim was thus to explore the feasibility of the use of the mild two phase procedure in benzylic bromination. In addition we also looked at the selectivity of the process and obtained evidence on the possible pathways for the formation of the different products.

Results and discussion

Benzylic bromination of toluene was initially performed in a biphasic system (H₂O–DCM), in order to optimize reaction

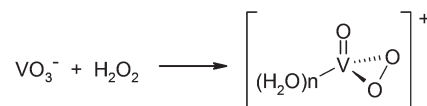
conditions. Vanadium catalysis was used, with H₂O₂ as a primary oxidant; for comparison purposes, the reaction was also investigated, under similar conditions, with a molybdenum catalyst. Ammonium vanadate (or ammonium molybdate) was the catalyst precursor, which was dissolved in water, with the pH value adjusted at 1.0. The nature of V species present was clearly confirmed by UV-visible spectra, since in acidic (pH = 1) aqueous solution, VO₃[−] with H₂O₂ formed almost exclusively the monoperoxido complex (λ_{\max} = 450 nm,¹⁵ Fig. ESI1†) also with a large excess of hydrogen peroxide (Scheme 2).

An analysis of absorption spectra of NH₄VO₃ and 2 equivalents of H₂O₂ at different pH values showed that at pH = 2, vanadium is present as both monoperoxido (λ_{\max} = 450 nm) and diperoxido (λ_{\max} = 350 nm¹⁵) complexes, according to the equilibrium in Scheme 3. At higher pH values, instead, diperoxido vanadium species is the only one present (Fig. ESI2†). Thus, pH = 1 was chosen as operative value, because diperoxido vanadium species was the most reactive in alkenes and alkynes oxybromination.^{5c,16}

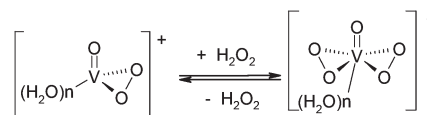
On the other hand, ammonium molybdate at pH = 1 with excess H₂O₂ was present only as diperoxido species (λ_{\max} = 340 nm,¹⁵ Fig. ESI3†), which underwent acid–base reaction in less acidic media, as indicated by the red shift of λ_{\max} (Fig. ESI4†).

The following reaction conditions were chosen: equivalent amounts of toluene and H₂O₂, a slight excess KBr, a sub-stoichiometric amount of the catalyst precursor, equal volumes of the two solvents (water and DCM), pH = 1 and *T* = 25 °C. Products analysis, performed at selected reaction times, indicated benzyl bromide as the main product, accompanied by small amounts of benzaldehyde and even smaller quantities of dibromo-methylbenzene (Scheme 4). An example of the reaction pattern is shown in Fig. 1.

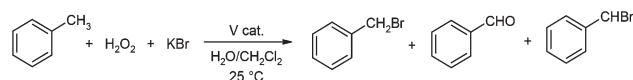
Different experiments were performed changing initial concentrations or the way hydrogen peroxide was added (at once



Scheme 2 Formation of monoperoxido V(v) species.



Scheme 3 Mono- and di-peroxido V(v) species in equilibrium at pH = 2.



Scheme 4 Product analysis of the V-catalyzed toluene oxidative bromination.

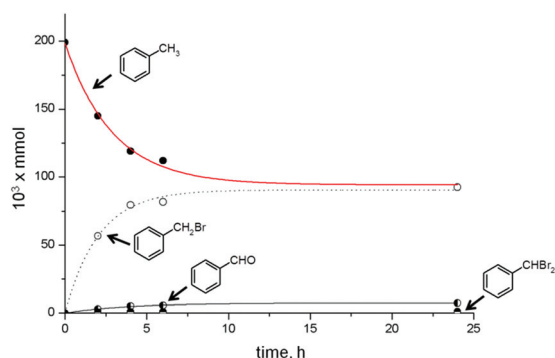


Fig. 1 V(v) catalysed toluene oxidative bromination in CH_2Cl_2 .

or in portions) and the same experiments were carried out with the molybdenum catalyst. The results from products analysis after 24 h are reported in Table 1; detailed information is given in the ESI.†

From inspection of Fig. 2, where the disappearance of toluene is reported vs. time, it is apparent that doubling the initial concentration of the bromide ion (Run 2) and even that of H_2O_2 (Run 3) did not affect the PhMe conversion significantly, unless H_2O_2 is added in two portions, the second one after 6 h (Run 4). Instead, doubling both KBr and H_2O_2 initial amounts (Run 5) increased decidedly the reactivity. The results are analogous when MoO_4^{2-} was used as the pre-catalyst, with an even faster PhMe consumption.

As for the products, the formation of benzyl bromide parallels the disappearance of toluene (Fig. 3), whilst benzaldehyde seems to form almost independently of reaction conditions (apart when an excess of H_2O_2 was present) and dibromomethylbenzene clearly forms slowly from benzyl bromide, being present in significant amounts only with an excess of the brominating reagent and the Mo pre-catalyst (Table 1, Run 5).

Generally, the Mo catalyst seems to give better results than the V one in terms of PhMe conversion, but this may be due to the V catalyzed H_2O_2 decomposition, which is faster with respect to that observed with Mo catalysis. As a matter of fact, starting from equimolar amounts of reactants, V was slightly more effective than Mo (Fig. 4, Run 1).

With a five-fold less vanadium precursor, the reaction still occurs (Run 6), but slows down. Formation of PhCHO seems to be less affected by the scarce amount of peroxy vanadate.

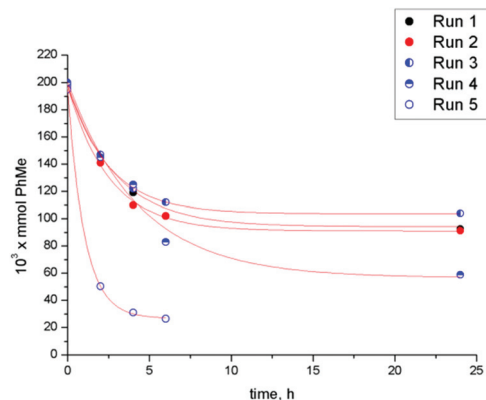


Fig. 2 PhMe conversion as a function of time, under the different reaction conditions in Table 1 (VO_3^- as a pre-catalyst).

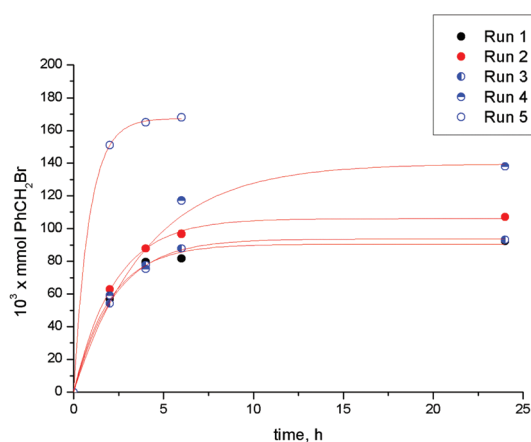


Fig. 3 Ph CH_2Br formation as a function of time, under the different reaction conditions in Table 1 (VO_3^- as a pre-catalyst).

Once the feasibility of the reaction had been ascertained, it was made more sustainable replacing the chlorinated solvent with the substrate itself. Toluene as the solvent/substrate also allowed us to perform the reaction at higher temperatures. With such a large substrate excess, dibromomethylbenzene was never observed (even in traces), whereas products from electrophilic aromatic bromination, *i.e.* *o*- and *p*-bromotoluene were found (Scheme 5).

An example of the reaction pattern is shown in Fig. 5.

Table 1 Toluene oxidative bromination with KBr and H_2O_2 in an $\text{H}_2\text{O}-\text{CH}_2\text{Cl}_2$ biphasic system after 24 h at 25 °C

#	KBr (mmol)	H_2O_2 (mmol)	VO_3^- (mmol)	% Conv. PhMe	Products (% rel)			MoO_4^{2-} (mmol)	% Conv. PhMe	Products (% rel)		
					Ph CH_2Br	PhCHO	Ph CHBr_2			Ph CH_2Br	PhCHO	Ph CHBr_2
1	0.25	0.2	0.1	53.5	92	7	1	0.1	42	91	9	Traces
2	0.5	0.2	0.1	54	93	5.5	1.5	0.1	71	90.5	7.5	2
3	0.25	0.4	0.1	47.5	96.6	2.5	1	0.1	66	90	8	2
4	0.25	0.2 + 0.2	0.1	71	93.5	4.5	2	0.1	84	91	5	4
5	0.5	0.4	0.1	90	91.5	2.5	6	0.1	88.8	66.5	1	32.5
6	0.25	0.2	0.02	37	86	12.5	1.5					

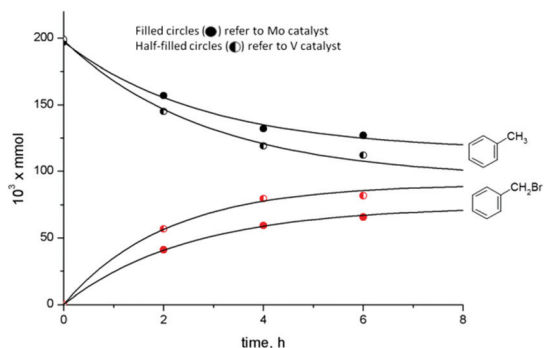
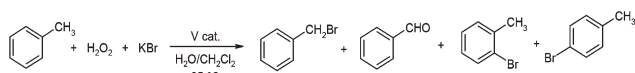


Fig. 4 Comparison between V and Mo catalysis in toluene oxidative bromination (Table 1, Run 1).



Scheme 5 Product analysis of the V-catalyzed toluene bromination in the biphasic system PhMe–H₂O₂.

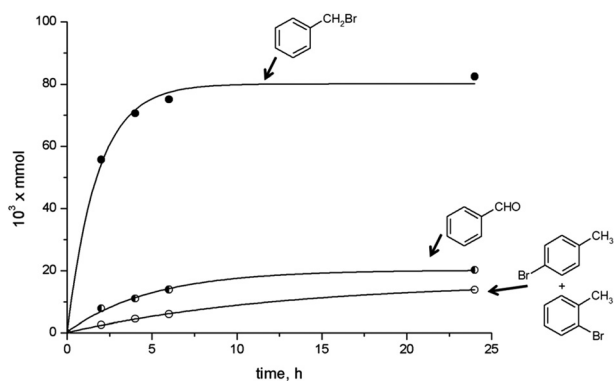


Fig. 5 Oxidative benzylic bromination reaction of toluene with V(v) catalysis in the biphasic system PhMe–H₂O₂.

Also in this biphasic system the reaction was repeated changing the initial conditions. Moreover, with toluene as the organic solvent, the temperature could be increased and runs at 40 °C were carried out as well. The results from products analysis after 24 h are reported in Table 2; detailed information is given in the ESI.† The formation of benzylbromide as a function of time and temperature is shown in Fig. 6.

Rising the temperature (Table 2, Run 2) accelerates H₂O₂ decomposition with VO₃[−], while with MoO₄^{2−} all products were formed faster, with a quantitative overall yield reached in 6 h,

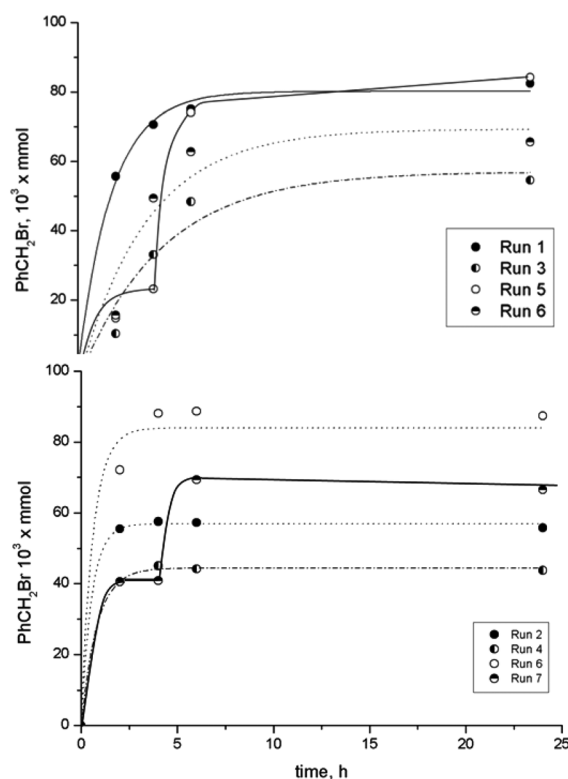


Fig. 6 PhCH₂Br formation as a function of time, under the different reaction conditions in Table 2 (VO₃[−] as a pre-catalyst), at 25 °C (above) and 40 °C (below).

Table 2 Toluene oxidative bromination with KBr and H₂O₂ in a PhMe–H₂O biphasic system after 24 h

#	T (°C)	KBr (mmol)	H ₂ O ₂ (mmol)	VO ₃ [−] (mmol)	%	Products (% rel)			MoO ₄ ^{2−} (mmol)	%	Products (% rel)		
						PhCH ₂ Br	<i>o</i> - + <i>p</i> -Br	PhCHO			PhCH ₂ Br	<i>o</i> - + <i>p</i> -Br	PhCHO
1	25	0.25	0.2	0.1	58.2	71	12	17	0.1	99	73	13	14
2	40	0.25	0.2	0.1	47.5	54	21	25	0.1	99.6 ^b	72 ^b	14.5 ^b	13.5 ^b
3	25	0.25	0.2	0.02	43.3	63	11	26	0.02	98.6	70	11	19
4	40	0.25	0.2	0.02	40.5	54	21	25	0.02	57.3	68	16	16
5	25	0.25	0.1 + 0.1	0.02	65.7	64	16	20	—	—	—	—	—
6	40	0.25	0.4	0.02	31.8	69	14	17	0.02	60.1	77	13	10
7	40	0.25	0.2 + 0.2	0.1	27.6 ^c	60	20.5	19.5	0.1	71.3 ^c	66	20	14
8	25	0.25	0.05 × 4 ^d	0.02	59.1	55.5	15	29.5	—	—	—	—	—
9	25	0.25	0.2	—	—	—	—	—	0.01	90	58.5	16	25.5

^a Relative to the limiting reagent (H₂O₂). ^b After 6 h. ^c Calculated on the basis of total H₂O₂ added. ^d Every hour.

Table 3 Recycle experiments in toluene oxidative bromination at 25 °C. PhMe–H₂O biphasic systems; 0.02 mmol NH₄VO₃. Each run after 24 h

Cycle	KBr	H ₂ O ₂	Overall yield (%)	Products relative %		
				PhCH ₂ Br	<i>o</i> - + <i>p</i> -Br	PhCHO
I	0.25	0.2	48	54.5	12.5	33
II	0.25	0.2	61	65.5	11	23.5
III	0.25	0.2	69	68.5	9.5	22

Table 4 Recycle experiments in toluene oxidative bromination at 25 °C. PhMe–H₂O biphasic systems; 0.02 mmol (NH₄)₂MoO₄. Each run after 24 h

Cycle	KBr	H ₂ O ₂	Overall yield (%)	Products relative %		
				PhCH ₂ Br	<i>o</i> - + <i>p</i> -Br	PhCHO
I	0.25	0.2	99	65	12	23
II	0.25	0.2	99	72	10.5	17.5
III	0.25	0.2	99	74	9.5	16.5
IV	0.25	0.2	96	75	13.5	11.5

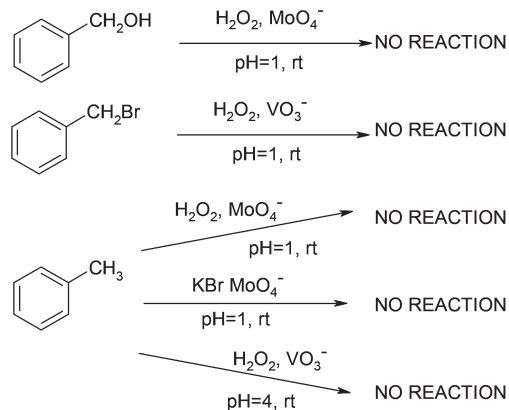
the relative percentage of products remaining the same as at 25 °C.

A decrease of the pre-catalyst amount (Table 2, Runs 4, 5 and 6) slows down the reaction with the V catalyst, whilst Mo is still highly efficient at 25 °C, in terms of the overall yield and selectivity (Table 2, Runs 3 and 9). With 1% molar, MoO₄⁻ the highest yield of PhCHO was observed.

Interestingly, catalysts recycling (with both vanadium and molybdenum species) was obtained by addition of fresh KBr and H₂O₂ to the biphasic toluene–water mixture, after 24 h.

Results collected in Tables 3 and 4 indicate that the MoO₄⁻ pre-catalyst is still highly efficient after 4 cycles; on the other hand, with vanadium catalysis, benzyl bromide is formed in higher amounts in subsequent runs, thus causing an increase of the overall yield. These data clearly add further value to the proposed two-phase procedure for toluene oxidative functionalization, even though, to render this approach practically applicable, further optimization is required.

Subsequently, experiments *ad hoc* were carried out in order to understand the mechanism of products formation. On the basis of data discussed in previous papers^{5,6} and illustrated in Scheme 1, the brominating reagent in the organic phase is mainly a bromine molecule, whereas oxidation is likely to occur at the interface. In fact, if dibromomethylbenzene reasonably derives from benzyl bromide and the latter might be produced by the well established mechanism of vanadium-catalyzed H₂O₂–Br⁻ reactions,^{5,7} benzaldehyde formation is quite puzzling. A reasonable path might be the hydrolysis of benzyl bromide to benzyl alcohol and subsequent oxidation in the oxidative medium. However, this route was ruled out, because, under the most efficient reaction conditions (PhMe–H₂O, H₂O₂, MoO₄⁻, pH = 1), benzyl alcohol remained unchanged in 24 h, with no traces of products whatsoever. Thus, PhCH₂OH is not an intermediate in the process leading to the aldehyde. Additional proof came from one experiment where benzyl bromide, in PhMe–water at pH = 1, in the

**Scheme 6** Tests for the formation of benzaldehyde in toluene oxidative bromination.

presence of VO₃⁻ and H₂O₂ – no Br⁻ added – gave neither hydrolysis product (no PhCH₂OH detected) nor PhCHO at all. To verify whether benzaldehyde could directly derive from toluene, a reaction was attempted under the standard conditions without bromide, but no oxidation products were detected.

Finally, toluene was treated with KBr and MoO₄⁻ – no H₂O₂ added – to look for any side reaction that might occur without the primary oxidant. Once again, no product at all was revealed (Scheme 6).

Quite recently, a mechanism was published related to benzyl alcohols or benzyl halides oxidation to aldehydes and ketones, with V₂O₅ and H₂O₂ at pH = 4.¹⁷ To note, those authors report in the text that a diperoxo vanadium species is operating with a nucleophilic character but the reactivity they observed is strongly enhanced at pH 1. Furthermore, when we treated toluene with H₂O₂–VO₃⁻ at pH = 4 (where diperoxo vanadium species is present), no reaction at all occurred. This is an expected result taking into consideration that an electrophilic reagent is at work.

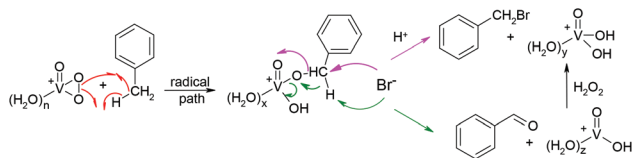
From a mechanistic point of view, also the formation of benzyl bromide is not easy to explain. Under the acidic reaction conditions used, hydride abstraction is highly unlikely as well as the proton dissociation. Thus, a radical pathway seems to be the most probable one,¹⁸ especially if a common intermediate can be envisaged for both benzyl bromide and PhCHO formation. As a matter of fact, when the reaction was carried out in the dark or in the presence of a radical scavenger (TEMPO), other conditions being equal, yield dropped with the VO₃⁻ pre-catalyst (less so with MoO₄⁻), as shown in Table 5.

From those data the relative % increase of aromatic bromination products is also clear, which is unaffected by the absence of light or the presence of radical scavengers, conditions that mainly hinder a radical route.¹⁹

To explain the observed behaviour, a possible path is shown in Scheme 7. Benzylic hydrogen abstraction by mono-peroxo V(v) species may give a reactive intermediate that undergoes nucleophilic displacement by the bromide anion,

Table 5 Toluene reaction with KBr (0.25 mmol) and H₂O₂ in a PhMe–H₂O biphasic system at 25 °C, after 24 h

H ₂ O ₂ (mmol)	Cat. (mmol)	Condition	Overall yield (%)	Relative %		
				PhCH ₂ Br	<i>o</i> - + <i>p</i> -Br	PhCHO
0.1 + 0.1	V (0.02)		63	62	19	19
0.1 + 0.1	V (0.02)	Dark	29	40	51	9
0.1 + 0.1	V (0.02)	TEMPO (0.1 mmol)	6.5	31.5	37	31.5
0.1 + 0.1	Mo (0.02)		99	70	11	19
0.1 + 0.1	Mo (0.02)	Dark	61.5	41	49	10
0.1 + 0.1	Mo (0.02)	TEMPO (0.1 mmol)	49	54	26.5	19.5

**Scheme 7** Proposed reaction scheme for benzylic bromination.**Table 6** Toluene reaction with different halides and H₂O₂ with the VO₃⁻ pre-catalyst (0.02 mmol), in a PhMe–H₂O biphasic system at 25 °C, after 24 h

H ₂ O ₂ (mmol)	Halide (mmol)	Yield (%)	Relative %		
			PhCH ₂ Br	<i>o</i> - + <i>p</i> -Br	PhCHO
0.1 + 0.1	KBr (0.25)	63	62	19	19
0.1 + 0.1	KF (0.25)	13	0	0	100
0.1 + 0.1	KCl (0.25)	7.5	0	0	100

thus yielding benzyl bromide. On the other hand, in nonpolar solvents Br⁻ may act also as a base, in a β-elimination path, which yields benzaldehyde and a V(IV) species, easily re-oxidized to V(V) by H₂O₂.²⁰

To verify the practicability of this hypothesis, the reaction was repeated changing the halide (Table 6).

With KF and KCl, PhCHO formed and was the only product observed. Therefore, the envisaged reaction pathway may be at work under our reaction conditions, although it might be not the only one operative. The selective formation of benzaldehyde in the presence of fluoride or chloride ions may derive from the expected enhancement of the basicity of the halides in a nonpolar medium such as toluene.

It is worth noting that the result with KF, where a reasonable amount of PhCHO formed, may open the way to a selective oxidation of toluene to benzaldehyde under mild, sustainable, and relatively inexpensive conditions, especially because yields may increase upon recharging the system with H₂O₂-KF, as suggested by recycling experiments.

Experimental section

¹H NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer, with CDCl₃ as a solvent. UV-visible spectra were

recorded on a SHIMADZU 2450 spectrometer equipped with the UV Probe 2.34 program. Gas-chromatographic analyses were carried out on a Varian 3900 instrument, with an FID 1770 detector and a 30 m Supelco SPB-5 column (0.25 mm diameter and 0.25 μm internal film). GC-MS spectra were recorded with a Shimadzu CP 6000 instrument, with a QP 5000 detector and a 30 m Supelco SPB-5ms column, of the same size as that used in GC.

All chemicals were of analytical grade and used without further purification. Dibromomethylbenzene (benzal bromide), necessary for quantitative determination, was prepared in 47% yield, from 102.3 mg (0.6 mmol) benzyl bromide, 178.5 mg (1.5 mmol) KBr, 53.5 mg (0.3 mmol) (NH₄)₂MoO₄, in a biphasic 1 : 1 v/v H₂O–CH₂Cl₂) upon addition of 115.2 μL (1.2 mmol) H₂O₂ followed by further 38.4 μL (0.4 mmol) after 24 h. After 72 h stirring at room temperature, when benzyl bromide completely disappeared, the organic phase was separated, washed with water, dried and evaporated. The crude benzal bromide was purified by column chromatography (SiO₂, eluent hexane).

Dichloromethane of commercial grade purity was purchased and used as such. Spectroscopic-grade solvents were used for UV-vis spectra. A commercially available aqueous solution of H₂O₂ was used after iodometric titration (10.4 ± 0.2 M H₂O₂ in water).

General procedure of biphasic bromination

For the reactions in H₂O₂–CH₂Cl₂, in a typical experiment, known amounts of KBr and ammonium vanadate, NH₄VO₃ (or ammonium molybdate, (NH₄)₂MoO₄) were dissolved with 10 mL distilled water and pH was adjusted to 1.0 with 86 μL 11.5 M perchloric acid. Toluene (2.0 × 10⁻¹ M) and decane (2.5 × 10⁻² M), as the internal standard, were dissolved in 10 mL dichloromethane. 1 mL of this mother solution was diluted to 10 mL with the same solvent. The aqueous and organic solutions were mixed in an Erlenmeyer flask, equipped with a magnetic stirrer and a condenser, to avoid evaporation. The biphasic system was stirred at 1000 rpm at room temperature. The necessary amount of H₂O₂ was added last, causing immediate formation of metal-peroxo species, as evidenced by the colour of the solution (deep red for mono-peroxido vanadium, yellow for diperoxido molybdenum). 100 μL of the organic phase were taken at selected times and examined using gas chromatography, injecting 1 μL. Periodical

controls for the presence of H₂O₂ were made with a starch-iodide paper. Quantitative analyses were performed with the aid of response factors determined for both reagents and products (see the ESI†).

Subsequently, the reaction was repeated changing one parameter at a time (reagents or catalyst concentration, temperature), as discussed in the appropriate section.

The reactions in H₂O₂-toluene were performed analogously, just weighing the internal standard and dissolving it with 10 mL toluene. Reactions at 40 °C were performed in thermostated vessels. All experiments were at least duplicated. For the table containing the experimental details, see the ESI.†

Blank experiments have been carried out without one reagent at a time (KBr or H₂O₂), in order to assess the importance of each species for the outcome of the reaction.

Conclusions

In conclusion the present work reports a vanadium and molybdenum catalysed sustainable oxidative bromination of toluene under very mild conditions (apart from pH) by using a cheap and efficient primary oxidant (H₂O₂) and a safe source of bromine equivalent reagents (KBr). The main achievements being: the possibility to eliminate chlorinated solvents from the reaction mixture and to recycle the catalytic phase without loss of efficiency, particularly with the Mo(vi) catalyst.

Benzyl bromides are attractive substrates for further utilization in synthetic procedures and the proposed reaction appears to be viable also with different benzylic substrates; the scope of the methodology is currently under analysis.

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