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## Vanadium-catalyzed, microwave-assisted oxidations with H<sub>2</sub>O<sub>2</sub> in ionic liquids\*

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**Abstract:** The application of vanadium(V) catalysts in selective oxidation with peroxides offers an efficient procedure that is compatible with different functional groups and leads to good yields and selectivities. However, the search for more efficient and sustainable procedures that employ H<sub>2</sub>O<sub>2</sub> as oxidant remains an important topic. In the last few years, striking results have been obtained by applying microwave (MW) activation in metal-catalyzed reactions carried out in ionic liquids (ILs). In the present study, results achieved with vanadium-based catalysts in oxidations of various substrates with H<sub>2</sub>O<sub>2</sub> are presented; in particular, epoxidation of alkenes and sulfoxidation of thioethers have been investigated. Notably, in the latter oxidation, a significant improvement in the rate of reaction and an increase in selectivity have been observed in the case of hydrophobic ILs in combination with MW activation.

**Keywords:** vanadium; oxidation; hydrogen peroxide; ionic liquids; microwaves.

### INTRODUCTION

Since the development of green chemistry there is a growing interest for more environmentally friendly and sustainable processes [1,2].

For economic and environmental reasons, oxidation processes with H<sub>2</sub>O<sub>2</sub> can be categorized as sustainable processes, taking into account that H<sub>2</sub>O<sub>2</sub> is, besides dioxygen, the most sustainable oxidant and the one with the highest “atom efficiency” (47 % of active oxygen). Furthermore, aqueous H<sub>2</sub>O<sub>2</sub> is readily accessible, safe to use, and leads to water as the only by-product [2–4]. Catalytic systems based on different metals have been employed in conjunction with H<sub>2</sub>O<sub>2</sub> for oxidation reactions [4].

In the perspective of more sustainable procedures, the reduction of the amount of volatile organic compounds (VOCs) used as solvents is of seminal importance. Recently, many research groups have

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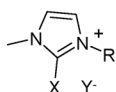
proposed new reaction media, ranging from fluorinated solvents [5], to supercritical CO<sub>2</sub> [6] and ionic liquids (ILs) [7,8]. Combinations of the latter two media have also been considered [9].

Our recent research focused on the use of ILs in metal-catalyzed oxidations with peroxides. ILs may be employed as sustainable alternative reaction media; they have negligible vapor pressure, they are stable, and they can be tailored for a specific reaction [10–13].

Oxidation reactions, and in particular catalytic versions thereof, often represent key processes to transform bulk chemicals into valuable materials. Millions of tons of such compounds are yearly produced worldwide and find applications in all areas of chemical industries [14]. Among these reactions, alkene epoxidation occupies a relevant position, since oxacyclopropanes are intermediates for both organic syntheses and industrial products, such as epoxy resins or paints. Top results obtained in the field of metal-catalyzed epoxidations in ILs have been collected in an excellent review [13]. Referring to epoxidation of simple olefins, reports have appeared using MeReO<sub>3</sub> [15], Fe<sup>III</sup> porphyrins under biphasic conditions [16], and Mn<sup>II</sup> in bicarbonate media [17].

Of continuing interest in the field of oxidative functionalization of hydrocarbons is the vanadium- and molybdenum-catalyzed oxybromination of alkenes and alkynes. In this respect, a simple and effective procedure for oxybromination of unsaturated substrates is the biphasic system H<sub>2</sub>O/CH<sub>2</sub>Cl<sub>2</sub>, proposed some time ago [18], where the catalyst, the oxidant, and potassium bromide are dissolved in the aqueous phase, while the substrate stays in the organic phase. Using this procedure, the activity of vanadium-dependent haloperoxidases [18a] was mimicked and, concomitantly, an interesting synthetic method for the functionalization of organic substrates under mild conditions was developed, with H<sub>2</sub>O<sub>2</sub>, and a sustainable source for bromine such as KBr.

Recently, a two-phase water/ILs oxybromination procedure for double and triple bonds with M/H<sub>2</sub>O<sub>2</sub>/Br<sup>-</sup> (M = V<sup>V</sup> or Mo<sup>VI</sup>) has been presented [18], and evidence was offered that an even more sustainable process, characterized by higher rates and better selectivity, was obtained. As an example, bmimPF<sub>6</sub>, bmimTf<sub>2</sub>N, and bdmimPF<sub>6</sub> (for abbreviations, see Scheme 1 below) provide very high yields and selectivity, up to 98:2 toward bromohydrin, in shorter reaction times [18a].



X	R	Y	acronym	hydrophilic
H	C <sub>2</sub> H <sub>5</sub>	[CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N] <sup>-</sup>	<b>emimTf<sub>2</sub>N</b>	<b>no</b>
H	C <sub>4</sub> H <sub>9</sub>	PF <sub>6</sub> <sup>-</sup>	<b>bmimPF<sub>6</sub></b>	<b>no</b>
H	C <sub>4</sub> H <sub>9</sub>	[CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N] <sup>-</sup>	<b>bmimTf<sub>2</sub>N</b>	<b>no</b>
H	C <sub>4</sub> H <sub>9</sub>	NO <sub>3</sub> <sup>-</sup>	<b>bmimNO<sub>3</sub></b>	<b>yes</b>
H	C <sub>4</sub> H <sub>9</sub>	CF <sub>3</sub> SO <sub>3</sub> <sup>-</sup>	<b>bmimTfO</b>	<b>yes</b>
H	C <sub>6</sub> H <sub>13</sub>	PF <sub>6</sub> <sup>-</sup>	<b>hmimPF<sub>6</sub></b>	<b>no</b>
H	C <sub>6</sub> H <sub>13</sub>	[CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N] <sup>-</sup>	<b>hmimTf<sub>2</sub>N</b>	<b>no</b>
CH <sub>3</sub>	C <sub>4</sub> H <sub>9</sub>	[CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N] <sup>-</sup>	<b>bdmimTf<sub>2</sub>N</b>	<b>no</b>
H	C <sub>3</sub> H <sub>6</sub> OH	[CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N] <sup>-</sup>	<b>HOpmimNO<sub>3</sub></b>	<b>yes</b>

Scheme 1

Another important topic in this field is the oxidation of sulfur-containing compounds, both from a synthetic point of view [19], i.e., the preparation of chiral sulfoxides and of sulfones, as well as considering modern processes for desulfurization of fuels [20]. Removal of sulfur from diesel oil and gasoline is becoming more and more important, not only to protect car exhaust catalysts, but also because of the more strict environment-protecting regulations. Up-to-date, hydrodesulfurization has been the

method of choice to remove thiols, sulfides, and disulfides, but it is not possible, by this process, to remove aromatic sulfur-containing compounds such as dibenzothiophene and 4,6-dimethyldibenzothiophene. To achieve ultra-deep desulfurization of fuels, oxidation reaction appears to be a promising procedure. Also in this field, ILs are employed, mainly as extractants [21]. The Brønsted acid IL, *N*-methylpyrrolidinium tetrafluoroborate, HmpBF<sub>4</sub>, was used both as extractant and as catalyst in oxidative desulfurization by H<sub>2</sub>O<sub>2</sub> [22]. Total removal of sulfur was achieved in the first run, with a slight decrease in efficiency after 10 cycles. Likewise, metal catalysis gave excellent results: Dibenzothiophene was oxidized by H<sub>2</sub>O<sub>2</sub>, with peroxotungsten and peroxomolybdenum phenanthroline complexes, in a number of ILs, resulting in 98 % removal of dibenzothiophene from model oil [23].

This background prompted us to explore the catalytic activity of selected vanadium complexes in oxidation reactions of various substrates, comparing organic solvents and ILs. In addition, microwave (MW) activation was applied with the aim to render the process even more synthetically interesting. In fact, recent reports [24] show the excellent results obtained in catalytic oxidations subsequent to the fast and efficient absorptions of MWs by ionic solvent phases.

## RESULTS AND DISCUSSION

Cyclooctene (COT) epoxidation was chosen as a model reaction for testing the reactivity of the selected vanadium complexes. Initially, the reactions were carried out at room temperature, using both hydrophilic and hydrophobic ILs\*, in order to establish if a homogeneous system performs better than a two-phase system. This last option derives, obviously, from the use of aqueous solutions of H<sub>2</sub>O<sub>2</sub> as primary oxidant. The ILs used were chosen on the basis of their stability in the presence of an oxidant and water. It has to be noted that, in several cases, irreproducible results were obtained by using commercial ILs. This fact, which has been ascribed to unknown impurities present in the samples, was addressed by several authors [10]. In order to ensure the high purity of the ILs, we decided to synthesize our solvents (see Experimental section for details). All the ILs synthesized and tested in this work are collected in Scheme 1.

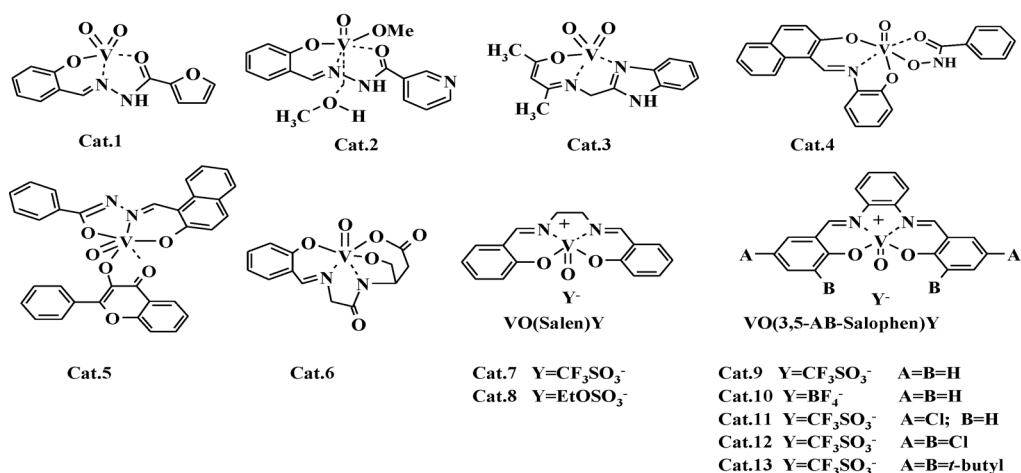
For most of the vanadium complexes studied, their performance as epoxidation catalysts was not well known. Thus, for the purpose of comparison, epoxidations in acetonitrile (MeCN) were carried out as well. Additionally, knowing that trifluoroethanol (TFE) is a very efficient solvent for oxidations by H<sub>2</sub>O<sub>2</sub>, the reactivity in this solvent was also briefly explored [25].

The complexes prepared and used in this work contained ligands based on different nitrogen/oxygen functional sets in the coordination sphere of vanadium, Scheme 2.

Both oxido and dioxido vanadium(V) species were considered. Planar and nonplanar vanadium settings were present in the salen and salophen derivative catalysts (cats.) **7–13**, and the hydrazone and Schiff-base cats. **1–6**. Some of these cats. (**1–3**) were previously prepared [26] to mimic the reactivity of the active site of vanadium-dependent haloperoxidases and have been found active in oxidation reactions in the presence of H<sub>2</sub>O<sub>2</sub>. Salen and salophen vanadium(IV) and -(V) derivatives have been synthesized in very good yields (see Experimental section), following slightly modified literature procedures [27], and identified by comparison of their properties with those published.

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\*The hydrophilic and hydrophobic nomenclature [10] is normally used in order to identify ILs which either form a single phase with water or dissolve only a very small quantity of water, respectively.



**Scheme 2** V(V) catalysts. The structures are based on XRD or proposed on the basis of spectroscopical data.

A preliminary screening of the reactivity of the vanadium complexes was carried out by analyzing the reactivity toward COT of cats. **2**, **3**, **6**, and **9** in the presence of H<sub>2</sub>O<sub>2</sub>, both in MeCN and in bmimPF<sub>6</sub>. Pertinent data are collected in Table 1. In MeCN, the epoxidation reaction was not very efficient, affording maximum 53 % of the COT epoxide in 5 h (with cat. **9**). Interestingly, for the first three complexes analyzed, a faster reaction was observed in bmimPF<sub>6</sub>. However, in general, compared to the literature [18], a synthetically interesting improvement of the yields was not observed. In the other hydrophobic ILs studied, much lower yields of COT epoxide were observed. Furthermore, no COT epoxidation was observed in hydrophilic ILs, such as bmimNO<sub>3</sub>, HOPmimNO<sub>3</sub>, and bmimTfO.

**Table 1** V-catalyzed epoxidation of cyclooctene (0.5 mmol) with H<sub>2</sub>O<sub>2</sub> (0.05 mmol)<sup>a</sup> in the presence of a V<sup>V</sup> catalyst (0.005 mmol) at room temperature.

Run	Complex	Solvent	Time <sup>b</sup> (h)	Yield <sup>c</sup> (%)
1	<b>2</b>	MeCN	24	7
2	<b>2</b>	bmimPF <sub>6</sub>	5	20
3	<b>3</b>	MeCN	24	0
4	<b>3</b>	bmimPF <sub>6</sub>	5	8
5	<b>6</b>	MeCN	24	33
6	<b>6</b>	bmimPF <sub>6</sub>	4	15
7	<b>9</b>	MeCN	5	53
8	<b>9</b>	bmimPF <sub>6</sub>	4	25

<sup>a</sup>1 ml of solvent.

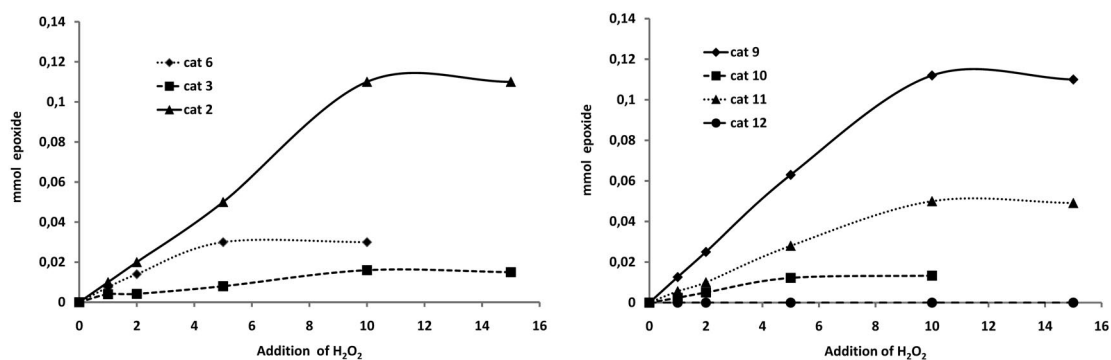
<sup>b</sup>At complete consumption of peroxide.

<sup>c</sup>Based on H<sub>2</sub>O<sub>2</sub>.

Variation of the reaction temperature, to 0 and 50 °C, resulted in a sharp decrease of the yield of epoxide. On the other hand, a small increase (up to 22 %) was observed, with cat. **3**, by increasing 10 times the COT concentration. In addition, increase of the initial concentration of H<sub>2</sub>O<sub>2</sub> resulted in a considerably less effective system (4 % yield of COT epoxide). Indeed, the vanadium-catalyzed decomposition of H<sub>2</sub>O<sub>2</sub> is a known process, and it appears that it is also operating under these conditions [28]. In order to overcome this problem, the vanadium-catalyzed (0.005 mmol) epoxidation of COT

(0.5 mmol) in  $\text{bmimPF}_6$ , by using equimolar amounts of  $\text{H}_2\text{O}_2$ , was carried out by adding the primary oxidant portion-wise to the reaction mixture. With this protocol, the final yield increased from 4 % (one single addition of  $\text{H}_2\text{O}_2$ ) to 20 % (10 successive additions). Under such conditions, the actual concentration of the peroxide in the solution is sufficiently low to assure that its decomposition does not compete efficiently with the epoxidation process.

On this basis, a screening of the reactivity of the complexes has been performed. Figure 1 shows the increasing amount of the COT epoxide as a function of the number of additions of  $\text{H}_2\text{O}_2$ . Catalyst **2** [ $\text{VO}(\text{OME})\text{sal-nah}(\text{HOME})$ ] (nah corresponds to the hydrazide of nicotinic acid) was more reactive in comparison to cat. **6**, [ $\text{VO}(\text{sal-glyser})$ ] ( $\text{H}_3\text{sal-glyser}$  is the Schiff base formed from salicylaldehyde and glycyserine), and cat. **3** [ $\text{VO}_2(\text{acac-ambmz})$ ], ( $\text{Hambmz}$  is the Schiff base derived from acetylacetone and 2-aminomethylbenzimidazole). Catalyst **2** exhibited a reactivity very similar to that of the unsubstituted salophen derivative cat. **9**. In all cases, interestingly, no formation of diol is observed.



**Fig. 1** V-catalyzed epoxidation of COT (0.5 mmol). Conditions:  $\text{H}_2\text{O}_2$  (0.05 mmol each addition), cat. (0.005 mmol); in 1 ml of  $\text{bmimPF}_6$ ,  $T = 25^\circ\text{C}$ .

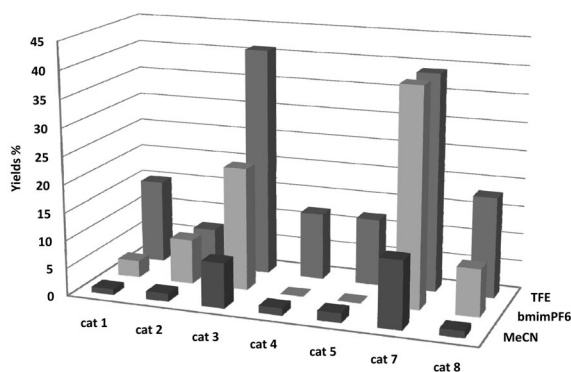
Quite surprisingly, electron-withdrawing groups in the periphery of the salophen ligands (cats. **11** and **12**, in Fig. 1) strongly diminish the catalytic activity of the vanadium complex toward double bonds. However, this aspect can also be attributed to faster decomposition of the peroxide. On the other hand, with cat. **13**, possessing four electron-donating groups in the salophen backbone, the observed reactivity toward COT was almost zero (not shown). In this latter case, the bulkiness of the ligand may heavily hamper the approach of the substrate to the peroxo complex, thus prevailing over the electronic effect.

At present, our results do not (yet) allow for a clear-cut correlation between the observed reactivity and the coordination environment of the metal center.

The difference in reactivity observed between cats. **9** and **10**, only the anion changes between them, can likely be ascribed to a different interaction (solvation) between the anions and the cationic partner of the solvent, which may affect the availability of the catalyst for reaction with  $\text{H}_2\text{O}_2$ .

A comparison has also been made between the reactivity of some of the synthesized complexes **1–5**, **7**, and **8** in MeCN and trifluoroethanol, TFE [25], a solvent known to activate  $\text{H}_2\text{O}_2$  in oxidation reactions (Fig. 2).

As can be seen in Fig. 2, with the exception of salen cat. **7**, the yields observed in TFE are definitely higher than those observed in MeCN and also in  $\text{bmimPF}_6$ . Nevertheless, the yields of COT epoxidation still remain quite low, and even though a further examination of the reactivity of vanadium complexes in TFE appears to be of importance, in this study the interest was very much focused on the use of ILs.

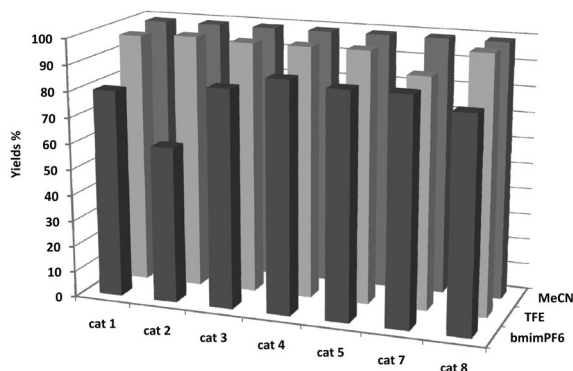


**Fig. 2** Solvent variation in the  $V^V$ -catalyzed epoxidation of COT = 0.5 mmol;  $H_2O_2$  = 0.5 mmol added in 10 portions; cat. = 0.005 mmol; solv. = 1 ml,  $T = 25\text{ }^\circ\text{C}$ ; complete consumption of the oxidant in about 6 h (each addition), yields are based on  $H_2O_2$ .

Other alkenes (cyclohexene and 1-octene) were much less reactive than COT. The activity of the vanadium catalysts was also probed toward other hydrocarbons. For adamantane, cyclohexane, and benzene, no formation of oxidized products was observed. Only traces of phenol were found with large excess of benzene and cat. 5.

Altogether, these results point to the presence of two competitive reactions: the oxidation of the substrate and the vanadium-catalyzed decomposition of  $H_2O_2$  [29]. Thus, in the presence of inadequately reactive substrates low yields of products are observed. In order to verify this hypothesis the attention was shifted toward the behavior of more reactive substrates. Thioethers were chosen considering the synthetic interest [19] for the preparation of sulfoxides and sulfones, as well as the processes for desulfurization of fuels [20].

As expected, in MeCN, TFE, and bmimPF<sub>6</sub>, using experimental conditions identical to those used for COT, the catalysts were very active in the sulfoxidation of thioanisole. However, quite surprisingly (see Fig. 3), the organic solvents gave better results in comparison with the IL bmimPF<sub>6</sub>. In general, only small amounts of overoxidized product were observed and the experimental conditions are definitely mild. Nonetheless, the reaction times (hours) are rather long for a synthetically useful procedure for thioether oxidation. To note, reactions in the absence of catalysts showed that TFE [25] and bmimPF<sub>6</sub> can activate  $H_2O_2$ , producing a small amount of sulfoxide (12 % in TFE in 24 h and 2 % in



**Fig. 3** Solvent variation in the  $V^V$ -catalyzed oxidation of thioanisole = 0.5 mmol;  $H_2O_2$  = 0.5 mmol added in 10 portions; cat. = 0.005 mmol; solv. = 1 ml,  $T = 25\text{ }^\circ\text{C}$ ; complete consumption of the oxidant in about 2 h (each addition), yields are based on  $H_2O_2$ .

bmimPF<sub>6</sub> in 120 h, at complete consumption of H<sub>2</sub>O<sub>2</sub>) while in MeCN, no formation of oxidized products is observed.

Therefore, in order to search for more efficient protocols, the oxidation of methyl *p*-tolylthioether in bmimPF<sub>6</sub> was considered (see Table 2).

**Table 2** V-catalyzed oxidation of methyl *p*-tolylthioether (0.5 mmol) with H<sub>2</sub>O<sub>2</sub> (0.5 mmol)<sup>a</sup> in the presence of a V<sup>V</sup> catalyst (0.005 mmol), in bmimPF<sub>6</sub>, at room temperature.

Run	Catalyst	Conversion <sup>b</sup> (%)	Sulfoxide (mmol)	SO:SO <sub>2</sub> <sup>c</sup>
1	<b>1</b>	>99	0.45	90:10
2	<b>2</b>	>99	0.43	86:4
3	<b>4</b>	>99	0.46	92:8
4	<b>5</b>	>99	0.45	90:10
5	<b>7</b>	>99	0.41	83:7
6	<b>13</b>	>99	0.40	80:20

<sup>a</sup>1 ml of bmimPF<sub>6</sub>.

<sup>b</sup>At complete consumption of peroxide ca. 3 h.

<sup>c</sup>Based on H<sub>2</sub>O<sub>2</sub>.

The data reported in Table 2 clearly show that this substrate is obviously more reactive than thioanisole, in accordance with the electrophilic nature of the process. However, the reaction time is still quite long (ca. 3 h) and more inappropriately, sulfone is also formed. To note, in the absence of catalysts, no substantial amount of oxidized products are formed in the same reaction time. The oxidation of this model sulfide was thus used to investigate the effect of the MW activation in such an ionic environment [24]. To this aim very low power was applied in order to limit the increase of the temperature in the reaction mixture, also considering that the response of ILs to MW activation is very effective. The results obtained are collated in Table 3 and indicate that in very short reaction times (seconds in comparison with hours) only the formation of sulfoxide is observed (MW power of 2 W).

**Table 3** Cat. **1** (μmol) catalyzed oxidation of methyl *p*-tolylthioether (1.86 mmol) with H<sub>2</sub>O<sub>2</sub> (0.125 mmol)<sup>a</sup>, in bmimPF<sub>6</sub>, with MW activation.<sup>b</sup>

Run	Catalyst (μmol)	Power (W)	Temperature (°C)	Conversion to sulfoxide <sup>c</sup> (%)
1	1.25	3	50	96
2	1.25	2	43	97
3	1.25	1	37	95
4	2.50	2	37	97
5	0.625	2	32	>99

<sup>a</sup>1 ml of bmimPF<sub>6</sub>.

<sup>b</sup>Complete consumption of peroxide 20 s.

<sup>c</sup>Based on H<sub>2</sub>O<sub>2</sub>, no sulfone is observed.

The absence of sulfone is to be expected considering the high ratio between substrate and primary oxidant. However, these conditions were chosen considering the optimization already done [24] in other oxidation reactions in ILs activated by MWs. Nonetheless, in the absence of catalysts, in otherwise identical experimental conditions only 60 % of sulfoxide was detected in 120 s (6 cycles of 20-s irradiation with 2 W power). The preliminary results reported in Table 3, even though the experimental con-

ditions are not directly comparable with those employed in the reactions of Table 2, point to the very high efficiency of MW activation in bmimPF<sub>6</sub> even at very low power. Furthermore, even lowering the amount of the catalyst to about five times full conversion and complete selectivity toward sulfoxide is detected in seconds (entry 5, Table 3).

The same conditions were used to test the reactivity of other vanadium complexes and in all cases very similar results were obtained (Table 4). Catalysts **1**, **2**, and **13** appear to be the best among those checked.

**Table 4** V-catalyzed (cat. = 0.625 μmol) oxidation of methyl *p*-tolylthioether (1.86 mmol) with H<sub>2</sub>O<sub>2</sub> (0.125 mmol)<sup>a</sup>, in bmimPF<sub>6</sub>, with MW activation (power 2 W).

Catalyst	Time (s)	Temperature (°C)	Conversion <sup>b</sup> (%)
<b>1</b>	20	32	>99
<b>2</b>	20	42	>99
<b>4</b>	100	37–46	92
<b>5</b>	80	38–46	93
<b>7</b>	40	43	97
<b>13</b>	40	43–49	>99

<sup>a</sup>1 ml of bmimPF<sub>6</sub>.

<sup>b</sup>Based on H<sub>2</sub>O<sub>2</sub>, no sulfone is observed.

In summary, interesting results with respect to the oxidation of methyl *p*-tolylthioether with H<sub>2</sub>O<sub>2</sub> in the presence of selected vanadium complexes have been presented. The scope of the reaction is likely to be wider, and thus further research is justified in order to explore the use of MW heating in oxidations carried out in ILs. The set of vanadium complexes investigated offers an excellent basis to study this effect and allow for optimization between H<sub>2</sub>O<sub>2</sub> decomposition and activation. The next step in process optimization would be to further lower the amount of catalyst and use equimolar amounts of substrate and oxidant in sulfoxidation.

## EXPERIMENTAL

**Caution:** The uncontrolled heating of large amounts of peroxides must be avoided. Care should be exercised in order to avoid possible explosion.

The synthesis of ILs used in this work was performed in a two-step procedure by quaternization of the alkyl-substituted imidazole with an alkyl-bromide followed by metathesis with a suitable anion [30]. The resulting ILs were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, and Fourier transform/infrared (FT/IR), and their identity was confirmed by comparison with literature data [31].

## Instruments

<sup>51</sup>V NMR spectra were recorded on a Bruker Avance 400 MHz, <sup>1</sup>H NMR spectra on a Bruker Avance 300 MHz spectrometer. GC analyses were carried out with a Shimadzu 2010 equipped with a 15-m capillary column EQUITYTM-5; or with a Varian CP3900 analyzer equipped with a 30-m capillary column Supelco SPB-1701. A CEM-DISCOVER reactor, equipped with a pressurized air system, was used to irradiate the reaction mixture. ChemDriver software was used to control parameters (power, pressure, and temperature). UV–vis spectra were recorded on a Varian Cary Scan 50 spectrometer. ESI/MS measurements were recorded on an LC/MSD spectrometer Agilent trap SL technology.



## Synthesis of ligands

Schiff bases used for the preparation of cats. **1–3** were prepared by following literature procedures [26]. For the preparation of H<sub>3</sub>sal-glyser=2-(2-hydroxybenzylideneamino)-N-(1-carboxy-2-hydroxyethyl)acetamide, see ref. [32].

### Synthesis of salen [1,2-bis-(salicylideneamino)-ethane] and salophen [1,2-bis-(3,5-AB-salicylideneamino)-benzene] ligands

*General procedure [26a]:* Two equivalents of the appropriate salicylaldehyde and one equivalent of the diamine was refluxed for about 30 min in the minimum volume of methanol. The solution was cooled to room temperature, and a yellow solid was precipitated. The solution was filtered, and the solid was purified by crystallization in ethanol. Salen [1,2-bis-(salicylideneamino)-ethane]: yield 83 %; <sup>1</sup>H NMR (300 Mhz, CDCl<sub>3</sub>): δ = 3.90 ppm (s, 4H, –CH<sub>2</sub>CH<sub>2</sub>–), δ = 6.84 ppm (t, 2H, H<sub>ar</sub>), δ = 6.93 ppm (d, 2H, H<sub>ar</sub>), δ = 7.21 ppm (d, 2H, H<sub>ar</sub>), δ = 7.28 ppm (t, 2H, H<sub>ar</sub>), δ = 8.33 ppm (s, 2H, –CH=N–), and δ = 13.2 ppm (s, 2H, –OH). Salophen [1,2-bis-(salicylideneamino)-benzene]: yield 95.3 %; <sup>1</sup>H NMR (300 Mhz, CDCl<sub>3</sub>): δ = 7.42–6.92 ppm (m, 12H, H<sub>ar</sub>), δ = 8.66 ppm (s, 2H, –CH=N–) and δ = 13.01 ppm (s, 2H, –OH); UV–vis in MeCN [ $\lambda_{\max}$ , nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 268 (23 200) and 329 (18 000)]; ESI/MS: *m/z* 317.3 = salophenH<sup>+</sup>. 5-Cl-Salophen [1,2-bis-(5-chlorosalicylideneamino)-benzene]: yield >99 %; <sup>1</sup>H NMR (300 Mhz, CD<sub>3</sub>CN): δ = 7.42–7.00 ppm (m, 10H, H<sub>ar</sub>), δ = 8.59 ppm (s, 2H, –CH=N–), and δ = 13.05 ppm (s, 2H, –OH); UV–vis in MeCN [ $\lambda_{\max}$ , nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 268 (18 300) and 340 (16 800)]. 3,5-Cl<sub>2</sub>-Salophen [1,2-bis-(3,5-dichlorosalicylideneamino)-benzene]: yield 95 %; UV–vis in MeCN [ $\lambda_{\max}$ , nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 270 (12 100) and 339 (8300)]. 3,5-di-*t*-butylsalophen [1,2-bis-(3,5-di-*t*-butylsalicylideneamino)-benzene]: yield 75 %; <sup>1</sup>H NMR (300 Mhz, CDCl<sub>3</sub>): δ = 1.20 (s, 18H, –C(CH<sub>3</sub>)<sub>3</sub>), δ = 1.40 (s, 18H, –C(CH<sub>3</sub>)<sub>3</sub>), δ = 7.20 – 7.60 (m, 8H, H<sub>ar</sub>), δ = 8.70 (s, 2H, –CH=N–), and δ = 11.70 (s, 2H, –OH).

### Synthesis of N-(2-hydroxyphenyl)-5,6-dibenzo-salicylideneamine, H<sub>2</sub>sal-anap

*Procedure:* 8.61 g (0.05 mol) 2-hydroxynaphthalene-1-carbaldehyde were dissolved in absolute ethanol (100 ml) and toluene (100 ml), under vigorous stirring and treated with 5.46 g (0.05 mol) *o*-aminophenol. The suspension was refluxed for 60 min to yield a deep red solution, from which the orange–red ligand crystallized during cooling. The product was collected by filtration, washed several times with cold ethanol and finally with hexane. The raw product was recrystallized from ethanol/hexane 3/1, and dried in vacuo. Yield 83 %; elemental analysis C<sub>17</sub>H<sub>13</sub>NO<sub>2</sub> (M = 263.32) found (calcd.): C 77.27 (77.55), H 5.19 (4.98), N 5.56 (5.32); selected IR data (KBr): 3026 (C–H<sub>ar</sub>), 1630 (C=N), 1599, 1585, 1514 (C=C), 1409 (OH) cm<sup>-1</sup>; <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): δ = 6.7–8.4 ppm (m, 10H, H<sub>ar</sub>), δ = 9.4 ppm (s, 1H, CH=N).

### Synthesis of 5,6-dibenzo-salicylidene-benzoylhydrazone, H<sub>2</sub>sal-hnap

*Procedure:* 5.17 g (0.03 mol) 2-hydroxynaphthalene-1-carbaldehyde were dissolved in ethanol (200 ml) and treated with a solution of 4.09 g (0.03 mol) of benzoic acid hydrazide dissolved in water (100 ml). This mixture was refluxed for 45 min, and cooled back to room temp. The solid thus obtained was filtered off, washed with water, ethanol, and hexane, and dried over P<sub>2</sub>O<sub>5</sub>. Yield 90 %; elemental analysis C<sub>18</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>·H<sub>2</sub>O (M = 308.34) found (calcd.): C 70.18 (70.12), H 5.26 (5.23), N 9.09 (9.09); selected IR data (KBr): 3480 (H<sub>2</sub>O), 3400, 3225 (N–H), 3059 (C–H<sub>ar</sub>), 1650 (C=O), 1622 (C=N), 1603, 1571 (C=C), 1409 v(OH) <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): δ = 7.21–8.24 ppm (m, 11H, H<sub>ar</sub>), δ = 9.49 ppm (s, 1H, CH=N).

## Synthesis of V<sup>IV</sup> complexes

### Synthesis of V<sup>IV</sup>O(salen)

The synthesis of these complexes was accomplished by following a procedure slightly different from that reported in the literature [27b,c]. Equimolar amounts of VO(acac)<sub>2</sub> and ligand were dissolved in the minimum volume of MeOH and after an overnight stirring in an open vessel the reaction was stopped. A dark green solid precipitated. Purification of V<sup>IV</sup>O(salen) was obtained by filtering the solution and washing the solid with methanol and diethyl ether. Crystals were dried by a vacuum pump. Yield 87 %. V<sup>IV</sup>O(3,5-di-*t*-butylsalophen) was purified [33] by dissolving the solid in ethanol. The solution was kept in a freezer for some days. The resulting precipitate was filtered by vacuum pump, washed with cold methanol and hexane, and dried. Yield >99 %.

### Synthesis of V<sup>IV</sup>O(salophen) and derivatives [27c,d]

*General procedure:* Equimolar amounts of V(acac)<sub>3</sub> and ligand were dissolved in the minimum volume of MeOH and after an overnight stirring in an open vessel the reaction was stopped. The solution was filtrated and crystals washed with methanol and diethylether. Samples were dried under vacuum. V<sup>IV</sup>O(salophen): yield 98.5 %; UV-vis in MeCN [ $\lambda_{\max}$ , nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>)] 312 (22 200) and 397 (17 700); ESI/MS:  $m/z$  381.1 = ML<sup>+</sup> (ML = complex). V<sup>IV</sup>O(5-Cl-salophen): yield 76.7 %, UV-vis in MeCN [ $\lambda_{\max}$ , nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>)] 305 (12 000) and 409 (10 700). V<sup>IV</sup>O(3,5-Cl<sub>2</sub>-salophen): yield 55 %, UV-vis in MeCN [ $\lambda_{\max}$ , nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>)] 315 (9800) and 412 (10 000).

## Synthesis of V<sup>V</sup> complexes

The synthesis of cats.1–3 has been reported previously [26].

### Synthesis of VO(sal-anap)pbha (cat. 4) and VO(sal-hnap)flav (cat. 5)

*General procedure:* 0.6 g (2.26 mmol) VO(acac)<sub>2</sub> were dissolved in warm ethanol (40 ml) and treated with 0.59 g (2.26 mmol) of the HONOH ligand in ethanol (20 ml). After stirring for 2 min, 2.26 mmol of the coligand (pbhaH or flavH) plus additional 20 ml of ethanol were added. The reaction mixture was heated to 50 °C and stirred for 80 min. The dark red–brown suspension thus obtained was cooled to room temperature, and the solid complex was recovered by filtration, several washings with ethanol and hexane, and drying in vacuo. VO(sal-anap)pbha: yield 76 %; elemental analysis C<sub>24</sub>H<sub>17</sub>N<sub>2</sub>O<sub>5</sub>V (M = 464.35) found (calcd.): C 62.28 (62.08), H 3.83 (3.69), N 5.85 (6.03); selected IR data (KBr): 3061 (C–H<sub>ar</sub>), 1617 (C=N), 1556 (C=O), 969 (V=O) cm<sup>-1</sup>; <sup>51</sup>V NMR (DMSO-*d*<sub>6</sub>):  $\delta$  = –442 ppm; <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 6.76–8.33 ppm (m, 15H, H<sub>ar</sub>),  $\delta$  = 9.80 ppm (s, 1H, CH=N). VO(sal-hnap)flav: yield 93 %; elemental analysis C<sub>33</sub>H<sub>21</sub>N<sub>2</sub>O<sub>6</sub>V·0.5EtOH (M = 615.59) found (calcd.): C 65.98 (66.35), H 3.85 (3.93), N 4.72 (4.55); elected IR data (KBr): 3066  $\nu$ (C–H<sub>ar</sub>), 1618  $\nu$ (C=N), 1541  $\nu$ (C=O), 1210  $\nu$ (V–OC<sub>flavone</sub>), 977  $\nu$ (V=O) cm<sup>-1</sup>; <sup>51</sup>V NMR (DMSO-*d*<sub>6</sub>):  $\delta$  = –433 ppm; <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$  = 7.24–8.56 ppm (m, 20H, H<sub>ar</sub>),  $\delta$  = 10.01 ppm (s, 1H, CH=N).

### Synthesis of VO(sal-glyser) (cat. 6)

The preparation by condensation of glycyserine (H<sub>2</sub>glyser) and salicylaldehyde (Hsal), in the presence of the oxidovanadium ion provided by vanadylsulfate in acetate-buffered methanol/water 2.5/1 under aerobic conditions was carried out in analogy to a published procedure [32]. The complex precipitates on addition of ether. Elemental analysis C<sub>12</sub>H<sub>16</sub>NO<sub>5</sub>V (M = 305.20) found (calcd.): C 47.10 (47.22), H 5.01 (5.28), N 4.76 (4.59). Selected IR data (KBr): 3435  $\nu$ (NH), 1682  $\nu$ (C=N), 1631  $\nu_{\text{as}}$ (CO<sub>2</sub><sup>-</sup>), 1546  $\nu$ (C=O)<sub>amide</sub>, 1401  $\nu_{\text{sym}}$ (CO<sub>2</sub><sup>-</sup>), 1297  $\nu$ (CN), 967  $\nu$ (V=O). <sup>51</sup>V NMR (CDCl<sub>3</sub>),  $\delta$  (relative intensity): –448 (1.4), –465 (2.3), –557 (1); i.e., in solution, three species are present with varying coordination modes of the ligand and/or nuclearity. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 8.06 ppm (s, 1H, CH=N),  $\delta$  = 8.30 ppm (d, 1H, CONHCH),  $\delta$  = 7.47–6.88 ppm (m, 4H, H<sub>ar</sub>),  $\delta$  = 4.31 ppm (s, 2H, NH<sub>2</sub>CO),  $\delta$  = 4.06–4.17 ppm (m, 3H, NCH<sub>2</sub>OH).

*Synthesis of VO(salen)CF<sub>3</sub>SO<sub>3</sub> and VO(3,5-AB-salophen)Y [A,B = H, Cl, t-butyl; Y = CF<sub>3</sub>SO<sub>3</sub>, BF<sub>4</sub>] [27d]*

*General procedure:* The desired amount of the appropriate V<sup>IV</sup> complex was dissolved in MeCN. An equimolar amount of acid (CF<sub>3</sub>SO<sub>3</sub>H or Ph<sub>3</sub>CBF<sub>4</sub>) was added. After some days the reaction was stopped and solvent evaporated to give a dark powder. The product was purified by a recrystallization from CH<sub>2</sub>Cl<sub>2</sub>-petroleum ether (Cats. **7** and **13**) or by a crystallization from CH<sub>2</sub>Cl<sub>2</sub>/MeCN (Cats. **9–12**). V<sup>VO</sup>(salen)CF<sub>3</sub>SO<sub>3</sub>: yield 87 %; <sup>51</sup>V NMR (400 MHz; MeCN): δ = -596.0 ppm. V<sup>VO</sup>(3,5-di-*t*-butylsalophen)CF<sub>3</sub>SO<sub>3</sub>: yield 80 %; <sup>51</sup>V NMR (400 MHz; MeCN): -594.2 ppm. V<sup>VO</sup>(salophen)CF<sub>3</sub>SO<sub>3</sub>: yield 37 %; <sup>51</sup>V NMR (400 MHz; MeCN): δ = -596.2 ppm; UV-vis in MeCN [ $\lambda_{\max}$ , nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>)] 306 (24 200) and 394 (5200). V<sup>VO</sup>(5-Cl-salophen)CF<sub>3</sub>SO<sub>3</sub>: yield 49.2 %; <sup>51</sup>V NMR (400 MHz; MeCN): δ = -595.6 ppm; UV-vis in MeCN [ $\lambda_{\max}$ , nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>)] 303 (21 300) and 408 (11 200). V<sup>VO</sup>(3,5-Cl<sub>2</sub>-salophen)CF<sub>3</sub>SO<sub>3</sub>: yield 42 %; <sup>51</sup>V NMR (400 MHz; MeCN): δ = -595.0 ppm; UV-vis in MeCN [ $\lambda_{\max}$ , nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>)] 313 (19 200) and 410 (13 700). V<sup>VO</sup>(salophen)BF<sub>4</sub>: yield 55 %; <sup>51</sup>V NMR (400 MHz; MeCN): δ = -588.6 ppm and -600.4 ppm; UV-vis in MeCN [ $\lambda_{\max}$ , nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>)] 307 (20 100) and 396 (9000).

*Synthesis of [V<sup>VO</sup>[(Salen)H<sub>2</sub>O][CH<sub>3</sub>CH<sub>2</sub>OSO<sub>3</sub>] (Cat. **8**) [34]*

*Procedure:* 0.5339 g (1.99 mmol) of ligand was dissolved in 7 ml of THF; 0.3880 g (2.38 mmol) of VOSO<sub>4</sub> was dissolved in 38 ml of hot ethanol. The two solutions were mixed and stirred under reflux for 24 h. The solvent was then evaporated and the residue purified by column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, then AcOEt/MeOH 2:1). Yield was about 20 %. <sup>51</sup>V NMR (400 MHz; MeCN): δ = -552.2 ppm.

## Oxidation with H<sub>2</sub>O<sub>2</sub>, catalyzed by V<sup>V</sup> complexes

### Reactions at room temperature

The catalyst was dissolved in the organic solvent (5 ml) or IL (1 ml). If necessary, ultrasound was used to promote catalyst dissolution. The substrate and H<sub>2</sub>O<sub>2</sub> were subsequently added. Reactions were carried out under vigorous stirring. Yields were calculated after complete consumption of the oxidant by GC quantitative analysis, using decane or dodecane as internal standard.

### Reactions with MW irradiation

The catalyst was dissolved in IL (250  $\mu$ l). If necessary, ultrasound was used to promote catalyst dissolution. The substrate and then H<sub>2</sub>O<sub>2</sub> were subsequently added. The reaction vessel was placed in the single-mode cavity of the instrument and irradiated with proper power, under simultaneous cooling by a stream of pressurized air (410 kPa pressure). Yields were calculated after complete disappearance of the oxidant, by GC quantitative analysis, with dodecane as internal standard.

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