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Oxidation of organic sulfides by a vanadium(5+) oxo–monoperoxo–picolinate complex: Kinetics and mechanism

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ABSTRACT

The kinetics of oxidation of p-X-benzyl phenyl- and p-Y-phenyl benzyl sulfides by V(V) oxo–monoperoxo complex [PicVO(O_2)] (Pic = picolinic acid anion) in acetonitrile at 20 °C is reported. The oxidation reaction leads to the formation of the corresponding sulfoxides and to oxygen produced from the oxidant decomposition started by the substrate. The change of the obtained sulfoxide-emitted oxygen ratio in p-Y-phenyl benzyl sulfides seems to be due to the substituent type used in the substrate, whereas when the substituent is isolated from the reaction centre, as in p-X-benzyl phenyl sulfides, the sulfoxide and oxygen emitted are not influenced by the substituent. Moreover the products obtained from the oxidation of some p-X-toluenthiols (the corresponding aldehydes) suggest the hypothesis of a possible pathway for the oxygen transfer step for these reactions. The process seems to require coordination of the organic sulfide to the metal, followed by oxidation within the coordination sphere.

1. Introduction

Vanadium chemistry has increasingly attracted attention as its involvement in biological systems has emerged as essential in recent years. The two predominant forms of vanadium occurring in the geo-, aqua- and biosphere, soluble and insoluble, are subject to bacterial activity and transformation. Bacteria belonging to genera such as *Shewanella*, *Psudomonas* and *Geobacter* can use vanadate as a primary electron acceptor in dissimilation or respiration and so on [1]. Coordination complexes of oxo–peroxo–vanadium(5+) played a key role in substrate oxidation for VHPOs (vanadium-dependent-haloperoxidase) [2]; in particular dioxovanadium (V) tripodal amine complexes K[VO(O_2)(heida)], with heida = (N-(2-hydroxyethyl)iminodiacetic acid), is the best oxidant (in terms of number of turnovers as well as rate) to convert organic sulfides into sulfoxides. The sulfide oxidation reaction is first order in substrate concentration. Electrophilic oxidation is proposed to proceed via the same mechanism as the halide oxidation with a protonated monoperoxovanadium complex, as the active species. Recently Pecoraro and co-workers [3] have shown that the oxo–monoperoxo–vanadium(5+) complex is capable to mimic bromide and thioether oxidation abilities of VHPOs, including the selective conversion, in nonaqueous solution, of thioethers to sulfoxides without over oxidation to sulfones. Moreover Abu-Omar and co-workers [4] have reported the first example of kinetics and mechanism of ligand substitution reactions involving oxo–diperoxo–vanadium compounds with ancillary ligands and small organic molecules [pic (picolinic acid) and dipic (dipicolinic acid)] as entering ligands at physiological pH. This result suggests that [VO(O_2)$_2$(bpy)]$^-$ is more prone to ligand substitution reactions and thus conversion to oxo–monoperoxo-species. The stabilities and ligand substitution kinetics of [VO(O_2)$_2$(bpy)]$^-$ and [VO(O_2)$_2$(phen)]$^-$ are markedly different, and this difference can be correlated to the difference in their DNA-cleavage activities. Some compounds of vanadium, in vitro, stimulate glucose uptake and inhibit lipid breakdown in a manner remarkably reminiscent of insulin's effects [5]. Kinetic studies on the oxidation of cysteine to cystine by four oxo–diperoxo-complexes of V(V) possessing insulin mimetic activity might suggest a coordination of cysteine to the metal, followed by oxidation within the coordination sphere. It can be suggested on the basis of some preliminary observations concerning the oxidation of $C_6H_5CH_2SH$ that the oxidation process is triggered by an electron transfer step [6]. Di Furia and co-workers [7] reported a kinetic study on the oxidation of di-n-butyl sulfide and phenyl methyl sulfide by two vanadium (V) peroxocomplexes [VO(O_2)OCH_3] and [VO(O_2)(PIC)(H_2O)$_2$] in methanol. The kinetic analysis of the reaction revealed that the first peroxo complex behaves as an electrophilic oxidant, whereas the second one acts as a radical oxidant.

Recently a series of new chiral oxovanadium(V) complexes like [VO(OMe)(L)] were synthesized [8]. The catalytic properties were investigated in the asymmetric oxidation of prochiral sulfides by organic hydroperoxides or hydrogen peroxide. The yield as well as the enantiomeric excess was found to strongly depend on the cat-

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alyst, on the substrate and on the oxidant [8a]. Particular attention has been paid to the factors that guide the discrimination between the two prochiral facies of the sulfides to steric implications deriving from the oxidant and from the specific complex used [8b].

In this paper, we report kinetic data concerning the oxidation of organic p-X-benzyl phenyl- and p-Y-phenyl benzyl sulfides with oxo–monoperoxo–picolinate vanadate(5+) [PicVO(O_2)] in acetonitrile at 20 °C and the oxidation of p-X-toluenthiols by [PicVO(O_2)] in acetonitrile at 10 °C. A plausible mechanism pathway for the oxygen transfer step is also proposed.

2. Experimental

2.1. Materials and methods

Thiophenol, 4-methoxythiophenol, 4-methylthiophenol, 4-chlorothiophenol, 4-nitrothiophenol, α-toluenethiol, 4-methoxy-α-toluenethiol, 4-chloro-α-toluenethiol, dibenzyl disulfide, benzylbromide, 4-fluorobenzylbromide, 4-methylbenzylbromide, 4-methoxybenzylchloride, 4-nitrobenzylbromide, benzaldehyde, 4-chlorobenzaldehyde, 4-methoxybenzaldehyde, vanadium(V) oxide, picolinic acid, and hydrogen peroxide (30%) are commercially available materials (Aldrich). Authentic samples of 4,4′-dimethoxydibenzyl disulfide and 4,4′-dichlorodibenzyl disulfide were prepared by oxidation (hydrogen peroxide 30%, H^+, ethanol) of the parent α-toluenethiol. Acetonitrile was purified by distillation over CaH_2 and stored over 4A molecular sieves. NMR spectra were carried on a 500-MHz Varian Unity Inova spectrometer equipped with pulse field gradient module (Z axis) and a tunable 5-mm inverse detection probe (ID-PFG). The chemical shifts (ppm) were referenced to TMS. The elemental analysis was obtained on a Fison CHNS Model EA 1108. Authentic samples of p-X-benzyl phenyl- and p-Y-phenyl benzyl sulfides were prepared by the reaction of the appropriate thiophenol with the appropriate benzylbromide in EtOH in the presence of KOH for 60 min at reflux; the products obtained were crystallized by methanol. The quantitative formation of the products in the oxidation reaction for α-toluenthiols was determined by HPLC (Jasco 880 PU with UV-VIS detector) employing a Nucleosil C18 column (150 mm × 4.6 mm) mobile phase acetonitrile/water (80/20) (flow rate = 1 mL/min, λ = 280 nm) and biphenyl as internal standard, and Varian 9010 equipped with a Varian 9050 UV-VIS detector, for the benzylphenyl sulfides employing a Hypersil column (250 mm × 4.6 mm), mobile phase, (A) CH_3CN, (B) H_2O and p-nitro-diphenyl sulfone as internal standard (flow rate = 1.2 mL/min, λ = 220 nm); gradient, 0–14 min 30% A, 14–50 min 100% A, 50–55 min 30% A. GC–MS analysis is performed for the characterization of disulfides and aldehydes in the oxidation reactions on a Hewlett-Packard Model 5890 gas chromatograph (using an HP-5 30 m capillary column) equipped with a Hewlett-Packard MS computerized system Model 5971A. A representative chromatogram is reported in Fig. 1.

The complex PicVO(O_2) was prepared by reported procedure [9]; the peroxide content was determined by cerimetric titration with a AMEL 333 pH-meter. Anal. (%) for $C_6H_4NO_5V{\cdot}2H_2O$, Calcd. *C* = 28.02, *H* = 3.11, *N* = 5.45. Found: *C* = 28.10, *H* = 3.15, *N* = 5.50. The amount of dioxygen evolved was determined by the means of a thermostated, 10-ml maximum capacity, gas burette. Kinetic measurements were performed by UV (PerkinElmer Lambda 2S and Beckmann DU 650 spectrophotometers) using 1 cm thermostatic quartz cells following the disappearance of the oxidant under pseudo first-order conditions. k_{obs} were determined using Guggenheim's method [10] because the oxidant dimer obtained as by-product absorb at the same wavelength of PicVO(O_2). All the products were characterized and identified on the basis of their spectral data [11].

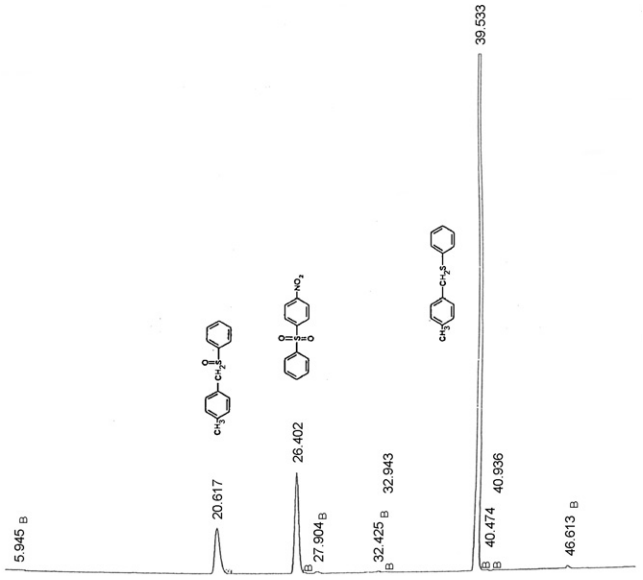


Fig. 1. HPLC for p-$CH_3C_6H_4CH_2SC_6H_5$ and PicVO(O_2) reaction.

4-Fluorobenzyl phenyl sulfide ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): 6.86–7.29 (m, 9H), 4.07 (s, 2H).

4-Nitrobenzyl phenyl sulfide ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): 8.11 (d, *J* = 9.0 Hz, 2H), 7.38 (d, *J* = 9.0 Hz, 2H), 7.23–7.29 (m, 5H), 4.13 (s, 2H).

4-Fluorobenzyl phenyl sulfoxide ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): 6.92–7.65 (m, 9H), 4.01 (d, *J* = 13.0 Hz, 1H), 3.98 (d, *J* = 13.0 Hz, 1H).

4-Nitrobenzyl phenyl sulfoxide ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): 8.08 (d, *J* = 9.0 Hz, 2H), 7.09–7.49 (m, 7H), 4.19 (d, *J* = 12.5 Hz, 1H), 3.99 (d, *J* = 12.5 Hz, 1H).

3. Results and discussion

3.1. Oxidation of p-X-benzyl phenyl sulfides

The oxidation of benzyl phenyl sulfides by PicVO(O_2) in acetonitrile at 20 °C gives the corresponding sulfoxides and dioxygen evolution (Scheme 1).

The kinetics was studied under pseudo-first-order conditions by using an excess of the substrate over the oxidant and was monitored following the oxidant disappearance through UV (λ = 453 nm). The observed rate constants k_{obs} (s^{-1}) were determined using the Guggenheim method [10]. It is known that in the absence of substrate, PicVO(O_2) decomposes quite rapidly yielding dioxygen and, likely, a V(V) dimeric species. The initiation involves two molecules of PicVO(O_2). In particular, one molecule acts as one-electron donor and the other one as one-electron acceptor, these pieces of information led to the proposal that PicVO(O_2) behaves as a radical oxidant

$$\text{p-X-C}_6\text{H}_4\text{-CH}_2\text{-S-C}_6\text{H}_5 + \text{PicVO}(\text{O}_2) \xrightarrow{\text{CH}_3\text{CN}} \text{p-X-C}_6\text{H}_4\text{-CH}_2\text{-S(O)-C}_6\text{H}_5 + \text{O}_2$$

$$\text{X}=\text{OCH}_3,\ \text{CH}_3,\ \text{H},\ \text{F},\ \text{NO}_2$$

Scheme 1.

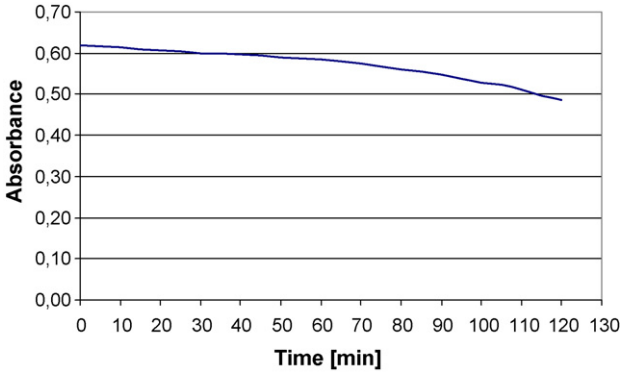


Fig. 2. [PicVO(O_2)] = 0.0016 M, CH_3CN, 20 °C, λ = 453 nm.

Table 1
Oxidation of substituted benzyl phenyl sulfides with PicVO(O_2) in CH_3CN at 20 °C.[a].

Entry	Substrates[b]	Sulfoxides (%)	O_2[c] (%)
1	$C_6H_5CH_2SC_6H_5$	$C_6H_5CH_2S(O)C_6H_5$ (67)	33
2	p-F-$C_6H_4CH_2SC_6H_5$	F-$C_6H_4CH_2S(O)C_6H_5$ (72)	28
3	p-NO_2-$C_6H_4CH_2SC_6H_5$	NO_2–$C_6H_4CH_2S(O)C_6H_5$ (71)	29
4	p-CH_3-$C_6H_4CH_2SC_6H_5$	CH_3–$C_6H_4CH_2S(O)C_6H_5$ (72)	28
5	p-CH_3O–$C_6H_4CH_2SC_6H_5$	CH_3O–$C_6H_4CH_2S(O)C_6H_5$ (71)	29

[a] The mmol of sulfoxides and O_2 were determined separately and no other product formation observed.
[b] In all experiments [Sub] = 0.016 M; [PicVO(O_2)] = 0.0016 M; t = 60 min; Conv. = 100%.
[c] Oxygen developed detected with a gas burette.

[9,12]. Fig. 2 shows the variation of absorbance as a function of time for PicVO(O_2) autodecomposition. As in all the considered oxidations the reaction time does not exceed 60 min, autodecomposition can be neglected and oxygen production is not due to autodecomposition but to reaction of the substrate.

In Tables 1 and 2 we report the quantitative analysis of products distribution and the rate constants, respectively. The quantity of oxygen and sulfoxide produced and the second order rate constants were not affected by the substrate substituents (Hammett plot with $\rho \approx 0$).

3.2. Oxidation of p-Y-phenyl benzyl sulfides

The oxidation of benzyl phenyl sulfides by PicVO(O_2) in acetonitrile at 20 °C gives the corresponding sulfoxides and dioxygen evolution (Scheme 2).

In Tables 3 and 4 are recorded the quantitative analysis of products distribution and the rate constants, respectively. As previously reported, the correspondent sulfoxides were obtained with oxygen production. The sulfoxide/oxygen production rates depend on substituents in the aromatic ring. In the case of p-$OCH_3C_6H_4SCH_2C_6H_5$ (Table 3) the (p-$OCH_3C_6H_4S$–)$_2$ is obtained as by-product. A more detailed analysis shows that electron-withdrawing substituents encourage sulfoxide formation, whereas the electron donating ones lower it correspondingly, increasing the oxygen quantity produced. The second order rate constants (Table 4) increase moving from electron withdrawing substituents to electron donating ones (Hammett plot with $\rho = -1.6$; Fig. 3). The p-NO_2 derivative second order rate constants could not be measured due to the low solubility of this compound above 0.03 M.

Table 2
Rate constants for the stoichiometric oxidation of substituted benzyl phenyl sulfides with PicVO(O_2)[a] in CH_3CN at 20 °C.

Entry	Substrates	×10^2 M	k_{obs}[b] (×10^4 s^{-1})	k_2[c] (×10^2 M^{-1} s^{-1})
1	p-CH_3O–$C_6H_4CH_2SC_6H_5$	6.01	10.6	
2		10.5	18.0	1.50
3		16.0	26.5	
4		20.0	31.6	
5	p-CH_3–$C_6H_4CH_2SC_6H_5$	3.18	6.17	
6		8.00	11.5	1.09
7		13.0	18.0	
8		18.0	22.0	
9	$C_6H_5CH_2SC_6H_5$	1.62	2.97	
10		3.23	5.91	
11		6.45	9.51	
12		9.03	12.3	1.07
13		13.1	17.0	
14		16.0	19.0	
15		20.0	23.0	
16	p-F-$C_6H_4CH_2SC_6H_5$	5.88	6.98	
17		10.1	10.9	1.12
18		12.5	14.3	
19		14.9	17.7	
20		19.9	23.5	
21	p-NO_2–$C_6H_4CH_2SC_6H_5$	1.63	5.00	
22		3.25	6.55	
23		6.54	11.6	1.53
24		13.4	22.2	
25		20.1	33.0	

[a] In all reactions [PicVO(O_2)] = 0.0016 M.
[b] Obtained with Guggenheim's method [10].
[c] Obtained from the slopes of plots of k_{obs} vs. [substrate]$_o$.

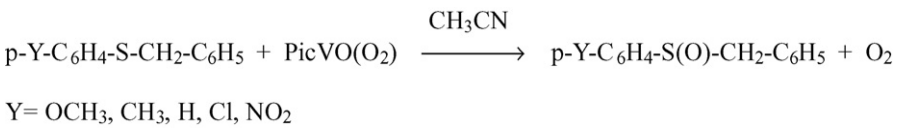
Table 3
Oxidation of substituted phenyl benzyl sulfides with PicVO(O_2) in CH_3CN at 20 °C.[a].

Entry	Substrates[b]	Sulfoxides (%)	O_2[c] (%)
1	$C_6H_5CH_2SC_6H_5$	$C_6H_5CH_2S(O)C_6H_5$ (67)	33
2	$C_6H_5CH_2SC_6H_4$–p-NO_2	$C_6H_5CH_2S(O)C_6H_4$–NO_2 (76)	24
3	$C_6H_5CH_2SC_6H_4$–p-Cl	$C_6H_5CH_2S(O)C_6H_4$–Cl (58)	42
4	$C_6H_5CH_2SC_6H_4$–p-CH_3	$C_6H_5CH_2S(O)C_6H_4$–CH_3 (50)	50
5	$C_6H_5CH_2SC_6H_4$–p-OCH_3[d]	$C_6H_5CH_2S(O)C_6H_4$–OCH_3 (25)	70

[a] The mmol of sulfoxides and O_2 were determined separately and no other product formation observed.
[b] In all experiments [Sub] = 0.016 M; [PicVO(O_2)] = 0.0016 M; t = 60 min; Conv. = 100%.
[c] Oxygen developed detected with a gas burette.
[d] 5% formation of $OCH_3C_6H_4SSC_6H_4OCH_3$.

Moreover the oxidation of p-X-toluenthiols by PicVO(O_2) (Fig. 4) in acetonitrile at 10 °C gives the corresponding disulfides and aldehydes with dioxygen evolution (Scheme 3).

The correspondent quantitative analysis of products distribution is reported in Table 5. The oxygen and diphenyl disulfide quantities obtained do not change the varying substituents, whereas p-substituted aldehydes were produced. The formation of C_6H_5CHO and O_2 could imply the intermediacy of the benzyl radical cation [p-X-$C_6H_4CH_2SH$]$^{+\bullet}$ and the radical anion of the oxidant [$VO(O_2)$(pic)]$^{-\bullet}$ [6].



Scheme 2.

$$\text{p-X-C}_6\text{H}_4\text{-CH}_2\text{-SH} + \text{PicVO(O}_2\text{)} \xrightarrow{\text{CH}_3\text{CN}} \text{X-C}_6\text{H}_4\text{-CH}_2\text{-S-S-CH}_2\text{-C}_6\text{H}_4\text{-X} + \text{O}_2 + \text{X-C}_6\text{H}_4\text{-CHO}$$

X= OCH_3, H, Cl

Scheme 3.

a) $\text{Sub} + \text{Pic-V(O}_2\text{)} \longrightarrow \text{Sub}^{+\bullet} + \text{Pic-V(O}_2\text{)}^{-\bullet}$

b) $\text{Sub}^{+\bullet} + \text{Pic-V(O}_2\text{)}^{-\bullet} \longrightarrow \text{Sub(O)} + \text{Pic-V=O}$

c) $\text{Pic-V(O}_2\text{)}^{-\bullet} + \text{Pic-V(O}_2\text{)} \longrightarrow \text{(Pic-VO)}_{\text{Dimer}} + \text{O}_2$

Scheme 4.

Table 4
Rate constants for the stoichiometric oxidation of substituted phenylbenzyl sulfides by PicVO(O_2)[a] in CH_3CN at 20 °C.

Entry	Substrates	$\times 10^2$ M	k_{obs}[b] ($\times 10^4$ s^{-1})	k_2[c] ($\times 10^2$ M^{-1} s^{-1})
1	$C_6H_5CH_2SC_6H_4$–p-OCH_3	1.76	9.41	
2		5.10	20.4	
3		10.0	31.7	
4		19.7	53.9	
5		25.1	73.5	2.79
6		38.2	106	
7		50.2	141	
8		60.4	174	
9	$C_6H_5CH_2SC_6H_4$–p-CH_3	1.69	4.59	
10		5.04	7.76	
11		10.5	17.6	1.58
12		21.1	33.7	
13		31.6	51.9	
14		43.3	69.1	
15		49.2	77.7	
16	$C_6H_5CH_2SC_6H_5$	1.62	2.97	
17		3.23	5.91	
18		6.45	9.51	
19		9.03	12.3	1.07
20		13.1	17.0	
21		16.0	19.0	
22		20.0	23.0	
23	$C_6H_4CH_2SC_6H_4$–p-Cl	1.91	1.69	
24		10.0	4.22	
25		19.9	10.0	
26		30.6	13.3	0.407
27		40.1	18.0	
28		50.1	19.8	
29		53.8	22.7	

[a] In all reactions [PicVO(O_2)] = 0.0016 M.
[b] Obtained with Guggenheim's method [10].
[c] Obtained from the slopes of plots of k_{obs} vs. [substrate]$_o$.

The product and second order rate constant analysis can be rationalized by the following mechanistic scheme (Scheme 4).

Association complexes between the aromatic substrates and oxo–diperoxo-complexes of Mo(VI), W(VI) and V(V) are reported in literature [6,13]. Step (a) preventing a coordination step between the metal and the substrate might precede the electron transfer process. During this step a water molecule, present in the metal coordination sphere, might be substituted by the substrate (Fig. 4).

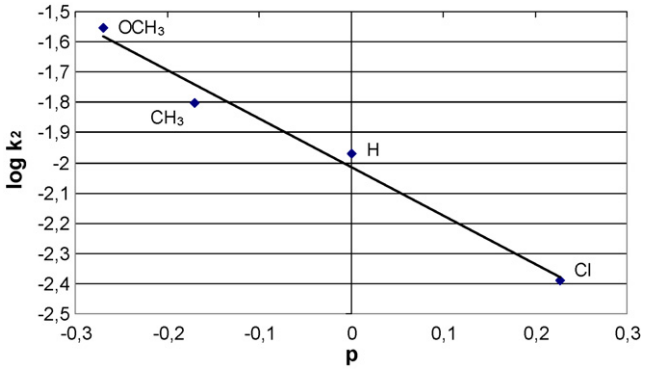


Fig. 3. Hammett plot of log k_2 vs. σ_p.

Moreover steps (b) and (c) are in competition for the reaction of the radical anion of oxidant [PicV(O_2)$^{-\bullet}$] formed in step a). It can either react with the substrate radical cation to give

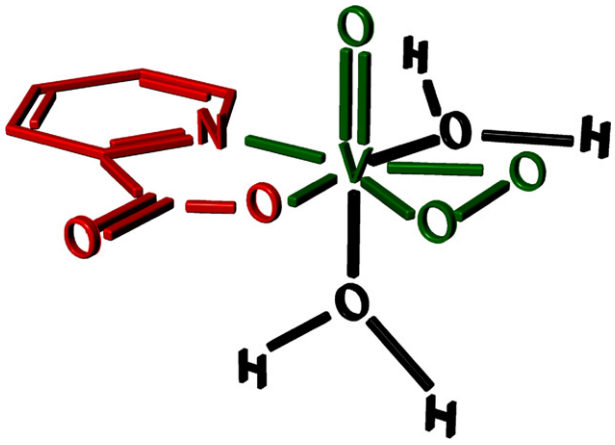


Fig. 4. Structure of PicVO(O_2).

Table 5
Oxidation of substituted benzylthyols with PicVO(O_2) in CH_3CN at 10 °C.

Entry	Substrates[a]	Products yields (%)	O_2[b] (%)
1	$C_6H_5CH_2SH$	$C_6H_5CH_2SSCH_2C_6H_5$ (43); C_6H_5CHO (22)	35
2	p-Cl–$C_6H_4CH_2SH$	$ClC_6H_4CH_2SSCH_2C_6H_4Cl$ (40); p-Cl–C_6H_4CHO (28)	32
3	p-CH_3O–$C_6H_4CH_2SH$	$CH_3OC_6H_4CH_2SSCH_2C_6H_4OCH_3$ (42); p-OCH_3–C_6H_4CHO (23)	35

[a] In all experiments [Sub] = 0.016 M; [PicVO(O_2)] = 0.0016 M; t = 15 min; Conv. = 100%.
[b] Oxygen developed detected with a gas burette.

sulfoxides (step b) or with the oxidant to form a dimer and oxygen evolution (step c) for which autodecomposition mechanism has been studied [12]. When the $-CH_2$ (X-C_6H_4–CH_2–S–C_6H_5 and p-X-C_6H_4–CH_2–SH) presence inhibits conjugation and therefore substituent electronic effects, the sulfoxides formation, oxygen evolution and rate constants are, within experimental error, equal for all substituted sulfides (Tables 1, 2 and 5). If electronic effects are present (p-Y-C_6H_4–S–CH_2–C_6H_5), products formation and rate constants are sensitive to substituent effects and consistent with the proposed mechanistic picture (Tables 3 and 4).

4. Conclusions

With this study we provide evidence that the thiol and sulfide oxidation by vanadium oxo–monoperoxo–picolinate complex may proceed by a SET mechanism. The information collected may be summarized as follows: PicVO(O_2) displays in CH_3CN a definite radical character when it acts as oxidant, the oxidizing species is a formal radical anion deriving from the transfer of one electron from the substrate to the oxidant. The mechanistic scheme proposed points out the (b) step determines the product formation as it is the only one that can be influenced by electronic effects of the substituents in the substrate.

Acknowledgements

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