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Oxo-metal complexes of alkoxo rich ligands and reactivity of vanadium complexes

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Abstract. Oxo-metal centers, such as, VO^{3+}, *cis*-VO_2^+, *cis*-MoO_2^{2+} and *trans*-UO_2^{2+} exhibited different coordination geometries and charge types to result in totally nine different types of structures, all of which were characterized by single crystal X-ray diffraction. Aqueous stability, reactivity towards acid, H_2O_2 and bromide of vanadium complexes are studied using absorption and ^{51}V NMR spectra. Catalytic nature of the bromination reaction by vanadium complexes has also been addressed.

Keywords. Vanadium complexes; NMR spectra; catalytic nature; bromination reaction.

1. Introduction

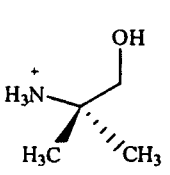
Schiff base and Mannich base ligands possessing varying number of alkoxo groups have been used extensively both by us [1] and others [2] in the literature in order to understand their coordination and biomimetic chemistry towards oxovanadium and oxomolybdenum centers in view of the importance of such oxo-metal motifs in biological systems [3]. However, in the biological systems, *cis*-dioxo motifs such as, VO_2^+, MoO_2^{2+} are predominant as cores of metalloproteins and metalloenzymes. As a part of our ongoing efforts in studying the biomimetic chemistry of oxo-metal complexes, the present paper deals with the structural variation found around VO^{3+}, *cis*-VO_2^+, *cis*-MoO_2^{2+} and *trans*-UO_2^{2+} moieties and further the solution stability and catalytic bromination activities of oxovanadium complexes.

2. Experimental

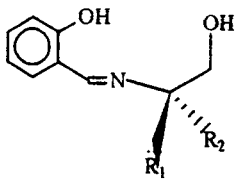
Stock solution of the vanadium(V) complexes were prepared in 0·05 M $HClO_4$ in DMF solutions. The bromination reactions were carried out after equilibrating for 30 min. Bromination of xylene cyanole was measured by monitoring the decrease in absorbance at 615 nm ($\Delta\varepsilon = 6000\ M^{-1}\ cm^{-1}$ at 0·05 M $HClO_4$) in the presence of KBr, H_2O_2 and V(V) complexes. Phenol red was incubated (*p*H 6·5) with KBr, H_2O_2 and V(V) complexes in $HClO_4$ (0·05 M) and the mixture was equilibrated for 3–30 min and the *p*H adjusted to 4·6. This mixture was assayed for bromination by monitoring a new absorbance band which appeared at 595 nm due to the formation of bromophenol blue. The synthesis of the V(V) complexes, [VO(*salamp*)(*Q*)], **1**, $[H_3O][VO_2(Q)_2]\cdot 2H_2O$, **2**, [*H*$_4$*amp*][$VO_2$

*For correspondence

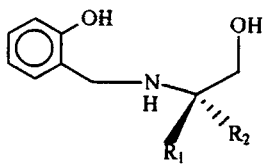
(*salampr*)], **3**, [VO(*Hsaltrisr*)]$_2$, **4**, [VO(*Hsaltris*)]$_2$, **5**, [*H*$_4$*amp*][VO$_2$(*salamp*)], **6**, [VO(*salamq*)(*cat*)], **7**, [VO(*hnanth*)(OMe)(MeOH)], **8**, and NH_4VO_3, **9** were reported earlier [1,4–6] and their solution stability in dmf-$HClO_4$ solution was followed using UV-VIS and ^{51}V NMR studies as reported in this paper. Structure and short names of ligands are provided in scheme 1.



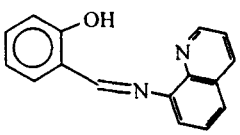
H4amp$^+$



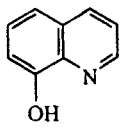
R1–R2–CH3 H2salamp
R1–R2–CH2OH, H4saltris



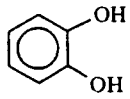
R1–R2–CH3 H2salampr
R1–R2–CH2OH, H4saltrisr



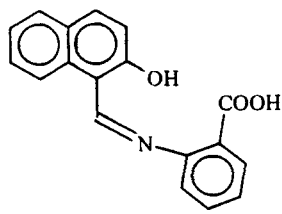
Hsalamq



HQ



H2cat



H2hnanth

Scheme 1. Labelling and structures of ligands used.

The addition of reagents was critical for exhibiting the bromination activity and the adopted protocol was followed to get reproducible results. The stock V(V) solution was prepared by equilibrating complexes **1–9** in dmf-$HClO_4$ for 30 min. The V(V) solution was then added to a reaction mixture containing the substrate (xylene cyanole or phenol red), H_2O_2 and excess KBr. Control experiments were performed in the absence of V(V) and/or H_2O_2 and also only in the presence of the ligand, *salamp*.

3. Results and discussion

3.1 *Structures*

Oxo-metal centres, such as VO^{3+}, *cis*-VO_2^+, *cis*-MoO_2^{2+} and *trans*-UO_2^{2+} exhibited different coordination geometries and charge types to result in totally nine different types of structures, all of which were characterized by single crystal X-ray diffraction. While vanadium exhibits both 5-coordinated and 6-coordinated structures, Mo and U exhibited only 6- and 7-coordinated complexes respectively [1,7]. Oxo-V(V) has shown some dinuclear structures, with a centrosymmetric V_2O_2 core and all the others showed mononuclear ones. Oxo-U(VI) shows dinuclear structures with centrosymmetric U_2O_2 core and only one of the CH_2O^- is involved both as binding and bridging, even when there are some unbound $-CH_2OH$ groups available in the complex. Instead of forming dinuclear structures, complexes of *cis*-MoO_2^{2+} picks up solvent molecules to result in

mononuclear complexes, even when there are some unbound $-CH_2OH$ groups available in the complex. In all the cases, the metal core geometries are highly distorted and range from trigonal bipyramidal to square pyramidal to octahedral to pentagonal bipyramidal types.

Expected changes were found in the bond distances of M=O, $M-O_{alk}$, and $M-O_{phe}$ on going from oxo-V(V) to oxo-Mo(VI) to oxo-U(VI) complexes. In all the *cis*-oxo-metal cores, the nitrogen from –HC=N– or $-H_2C-NH-$ group of the ligand occupies a near *trans*-position to M=O bond. This is understandable from the correlation obtained between the M=O distance and O=M–N angle. The O=M–N angle varies between 120–160° in various oxo-V(V) and oxo-Mo(VI) complexes. However, this is not true in the case of uranium complexes as the metal center has *trans* dioxo geometry.

3.2 *Reactivity*

In order to understand the reactivity of the oxo-vanadium complexes, we have studied their solution speciation and their catalytic bromination towards different substrates.

(a) *Reactivity with H_2O.* The solution stability properties of complexes **1–9** was studied in the presence of added water, $HClO_4$ or H_2O_2 and the reactions were monitored using UV-VIS and ^{51}V NMR spectra. Complexes **1–3**, **5**, **6**, **8** and **9** were found to be stable over a period of 48 h in 4:1 dmf:H_2O solvent mixture. However, complex **4** decomposes even in the presence of one equivalent of water and gives rise to a mixture of vanadates. In the presence of one to four equivalents of water, **7** is converted to the tbp *cis*-VO_2(*salamq*) by the loss of the bidentate catechol ligand, as monitored by the disappearance of the ^{51}V NMR signal at 323·1 ppm (of **7**) and appearance of a new signal at –535·4 ppm[5]. This conversion was also studied using UV-VIS absorption spectra, where the low energy bands at 864 nm and 530 nm in complex **7** slowly disappear and gives rise to a new band at 430 nm. VO_2(*salamq*) complex was found to be stable under these conditions for over 48 h[8].

(b) *Reactions with H_2O_2*: Complexes **3** and **6** on reacting with H_2O_2 (1:4 to 1:10, complex: H_2O_2) under neutral conditions, showed a gradual decrease in the intensity of the band at 360 nm which finally disappears. A new band at 410 nm appeared, which increased in intensity as a function of time. Three isosbestic points at 300, 330 and 395 nm were observed during the progress of the reaction indicating an equilibrium between the complex and the free Schiff base in solution. When ratios of less than 6:1 H_2O_2:V are used, the band at 360 nm does not disappear completely. The equilibrium is shifted towards complex formation after about 60–120 min with an inverse dependence on the amount of H_2O_2 added.

From the reaction of **6** with a ten-fold excess of H_2O_2, a complex was isolated which did not contain the Schiff base bound to the metal center and was identified as a simple oxoperoxovanadium(V) species[4]. Similar observations were made under acidic dmf (0·05 M $HClO_4$ in dmf), but the rate of formation of the oxoperoxovanadium(V) species was faster and irreversible, probably due to the instability of the Schiff base under acidic conditions. Complex **1** reacts with H_2O_2 in 1:8 and 1:10, ratios under neutral conditions to give a mixture of the dioxovanadium(V) complex, **6** and free HQ ligand. After the generation of **6** from the reaction of **1** and H_2O_2, this system behaves similar to the one observed during the reaction of **6** with H_2O_2. Complex **2** reacts with H_2O_2 under similar

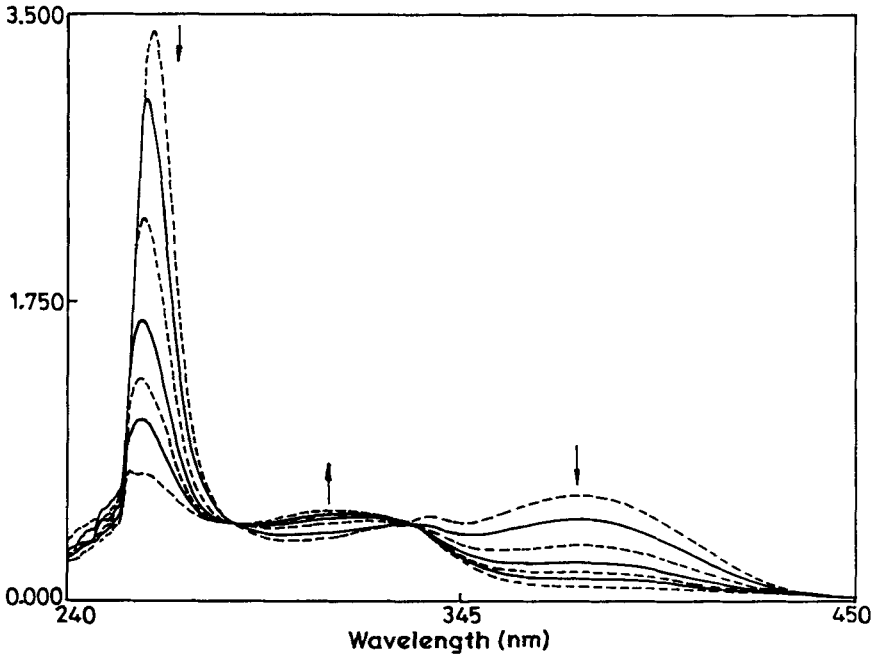


Figure 1. UV-VIS spectra of a reaction mixture of **2** and H_2O_2 (1:8) as a function of time over a period of 30 min.

experimental conditions and shows two isosbestic points (figure 1) at 330 nm and 286 nm. Complexes **5**, **8** and **9** did not react with H_2O_2 under similar experimental conditions. However, complex **4** on the other hand forms a mixture of vanadates and < 5% oxoperoxo-vanadium species after about 72 h on treatment with H_2O_2 in excess amounts (20:1 of H_2O_2:V). Under lower proportions of H_2O_2 (< 6 equivalents), the complex decomposes to give a mixture of vanadates, as was observed during the reaction of **4** with water.

(c) *Reactions in the presence of acid:* Addition of HCl to the reaction mixture containing **1** and H_2O_2, led to the disappearance of the 354 nm band and a new band at 320 nm appeared. Two isosbestic points at 330 and 301 nm were observed over a period of 20–30 min as shown in figure 2 a. Addition of NEt_4Br to the above reaction mixture led to an increase in the intensity of 320 nm band over a period of 20 min as shown in figure 2 b. This increase in intensity has been attributed to the formation of an equilibrium mixture of OBr^-, Br_2 and Br_3^-.

When complex **1** was treated with 0·05 M $HClO_4$ in dmf the original bands at 510 nm disappeared within 12–15 min and new bands appeared at 351, 277 and 260 nm. Addition of ten-fold excess of H_2O_2 to the above reaction mixture led to an increase in the intensity of the 277 nm band. The other band at 351 nm remained unaltered. Treating complex **2** with 0·05 M $HClO_4$ in dmf results in the formation of bands at 353, 320 and 309 nm within 30 min. However, equilibrium exists in solution and the regeneration of complex **2** was observed with the formation of bands at 378 and 337 nm after about 60–90 min. On treatment of **2** with 0·5 M $HClO_4$ in dmf, the regeneration of the complex is completely

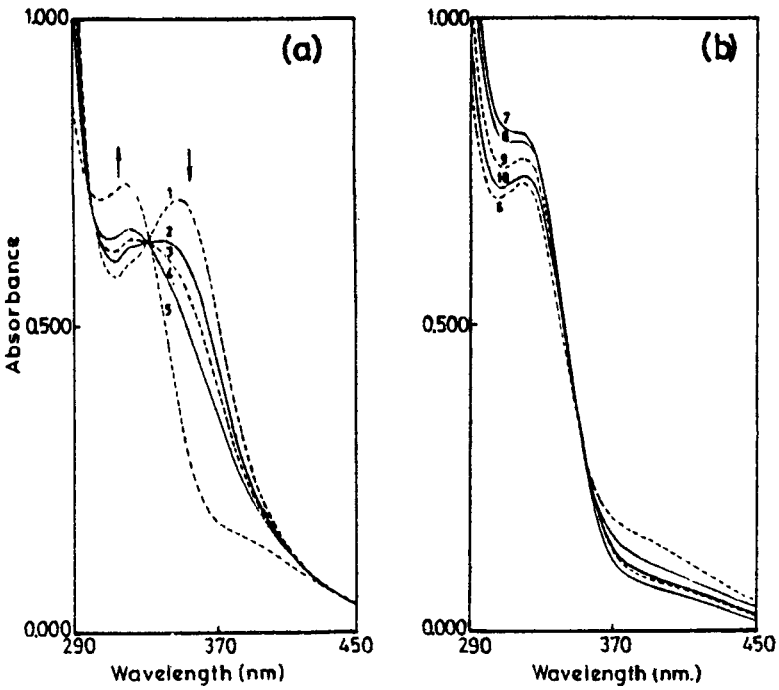


Figure 2. Absorption spectra as a function of time: (**a**) of the mixture of **1** + H_2O_2 + HCl; (**b**) of that in (**a**) + Et_4NBr. Spectra are recorded at: (1) 0; (2) 2; (3) 5; (4) 8; and (5) 20 min in case of (**a**); and (6) 0; (7) 2; (8) 9; (9) 14 and (10) 20 min in case of (**b**).

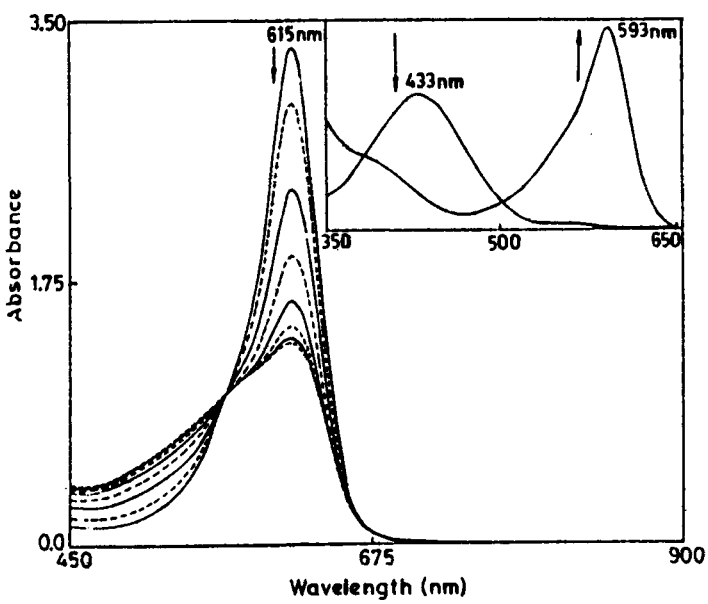


Figure 3. Absorption spectra of bromination of (**a**) Xylene cyanole by *cis*-VO_2^+ generated from a mixture given in figure 2(b), Inset: bromination of phenol red by the same reaction mixture.

inhibited. Addition of ten-fold excess of H_2O_2 to the reaction mixture containing **2** and 0·05 M $HClO_4$ in dmf led to the observation of a broad band at 353 nm. On equilibration of complex **4** with dmf-$HClO_4$ for 10–15 min, a decrease in the intensity of the 474 nm band was observed and the intensity of the other bands at 275 and 257 nm increased. On addition of ten-fold excess of H_2O_2, only one band at 262 nm and a shoulder at 350 nm were observed. Similar observations were made upon the treatment of **5** with 0·05 M $HClO_4$ in dmf, though the time taken for the complete disappearance of the low energy band was about 45 min. When complex **8** was treated with 0·05 M $HClO_4$ in dmf, the original bands at 560, 429 and 327 nm disappeared and new bands appeared at 429, 344, 318 and 261 nm. Addition of ten-fold excess of H_2O_2 to this reaction mixture led to the formation of bands at 319, 263 nm and a shoulder at 354 nm persists. On treating complex **9** with 0·05 M $HClO_4$ in dmf, broad bands at 287 and 334 nm were observed. Treating this reaction mixture with a ten-fold excess of H_2O_2 gave rise to a band at 290 nm with a shoulder at 348 nm. In general it was observed that the reaction of various V(V) complexes with 0·05 $HClO_4$ in dmf led to disintegration of the complex. However, common bands at 345 ± 5 nm were observed upon addition of H_2O_2 to the above reaction mixtures, in all the complexes.

(d) *Reactivity by UV-VIS spectra:* Equilibration of the complexes **1–9** in 0·05 M $HClO_4$-dmf solution for 10–30 min ensures the formation of *cis*-VO_2^+ species. The original absorption bands disappear and new bands which are common to all V(V) complexes were observed at 270 ± 10 nm and 350 ± 15 nm. Addition of H_2O_2 to the above solution lead to an increase in the absorption of the former band at 270 ± 10 nm, while the latter at 350 ± 15 nm is mostly unaffected. Addition of Et_4NBr or KBr to the reaction mixture containing VO_2^+ and H_2O_2 in dmf-$HClO_4$ leads to an increase in the intensity of the absorbance of the 350 ± 15 nm band.

(e) *Reactivity by ^{51}V NMR spectra and mechanistic aspects:* The ^{51}V NMR chemical shifts of **1–9** in 0·05 M $HClO_4$-dmf showed signals around –485 ± 5 ppm. In case of complex **2**, two signals in the ratio 3:2 were observed at –483 and –517 ppm, indicative of an equilibrium mixture of *cis*-VO_2^+ and the V(V) complex, $[VO_2(Q)_2]^-$. Addition of excess of H_2O_2 (10–50 fold excess) resulted in the formation of sharp signals within 10 min at –550 ± 10 and –650 ± 15 ppm in a 1:1 ratio, with an additional downfield signal at –485 ± 5 ppm. Another signal at –630 ± 2 ppm was observed after 15–30 min of equilibration at the expense of the –550 ± 10 and –650 ± 15 ppm signals. Addition of KBr to this mixture leads to a rapid disappearance of the –630 ± 2 ppm signal and appearance of a new signal around –560 ± 5 ppm. While this signal cannot arise from a directly bonded V–Br species as expected based on the inverse electronegativity relation of ^{51}V NMR chemical shifts, the same may have originated from **"V–OBr"** species. The intensity of the latter signal decreases eventually and the peaks at –550 ± 10 and –650 ± 15 ppm reappear in equilibrium with the –485 ± 5 ppm signal. In case of complex **2**, the equilibrium mixture of *cis*-VO_2^+, $[VO_2(Q)_2]^-$, $VO(O_2)^+$ and $VO(Q_2)_2^-$ has been identified through the ^{51}V NMR signals at –483, –521, –550 and –654 ppm in a 2:1:2:2 intensity ratio. The ^{51}V NMR spectra of complex **2** in dmf in the presence of H_2O_2 and KBr as a function of time is shown in figure 4. Complex **2** in dmf or dmso gives one sharp signal at –520·5 ppm. However in case of the other V(V) complexes, **1**, **3–6**, **8** and **9** the regeneration of the V(V) complex does not take place, probably due to the cleavage or disintegration of the ligand in highly acidic conditions. In any case, the generation of

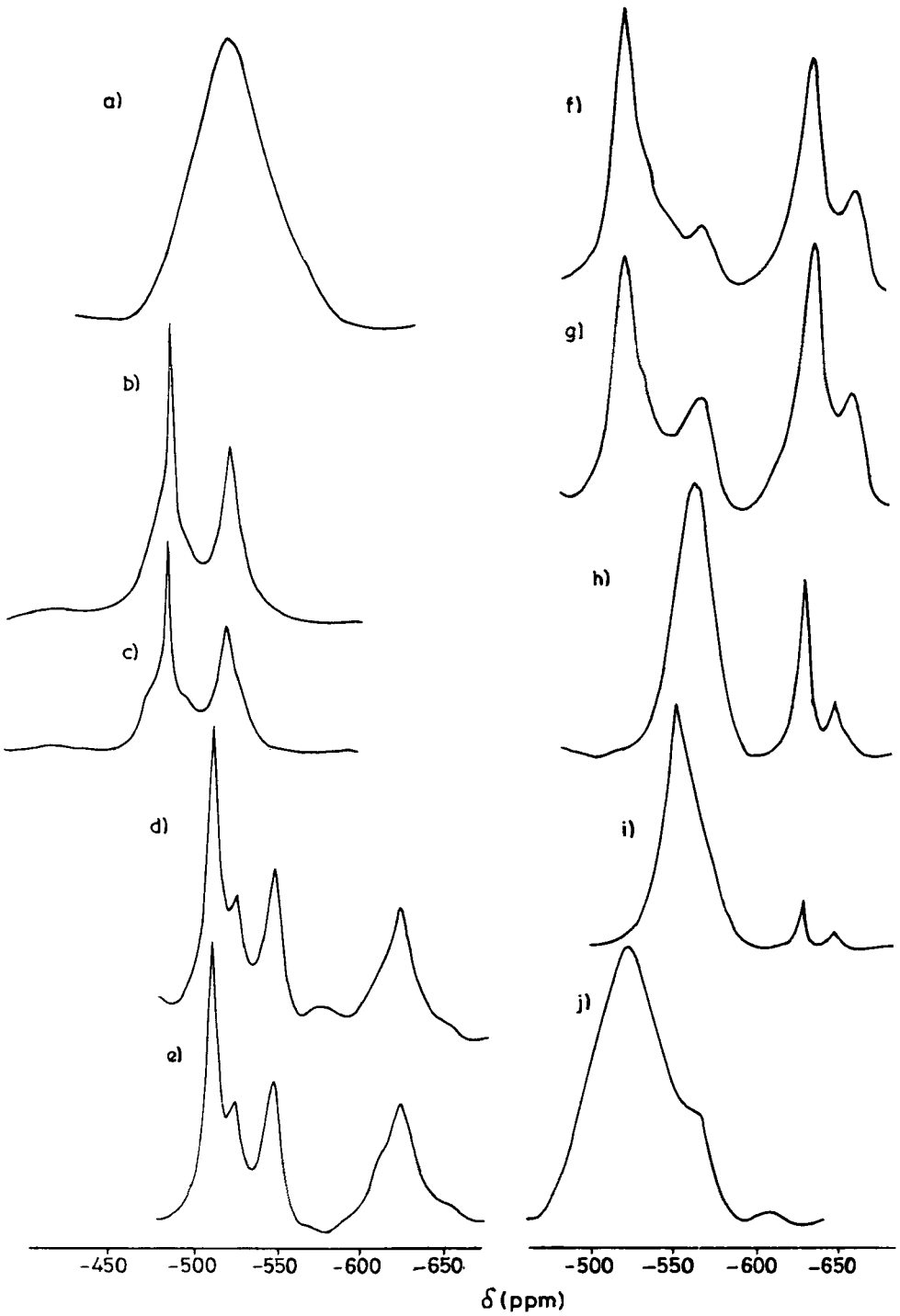
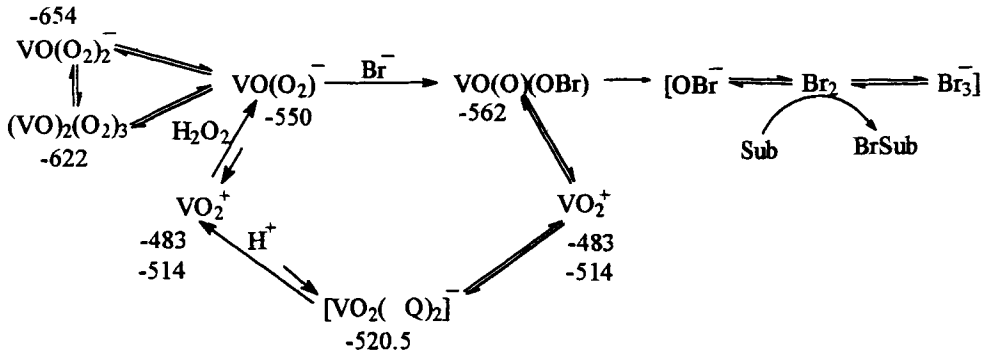


Figure 4. ^{51}V NMR spectra of the reaction between complex **2** and H_2O_2 and KBr as a function of time (**a**) Complex **2** in dmf; (**b**) a + $HClO_4$, 11 min; (**c**) 21 min; (**d**) c + H_2O_2, 1 min; (**e**) 10 min; (**f**) 30 min; (**g**) f + KBr, 1 min; (**h**) 10 min; (**i**) 30 min and (**j**) 60 min.



Scheme 2. Experimentally observed steps during the bromination reaction of **2**. Correct species among those shown in brackets is not fully conformed. The numerical values indicate ^{51}V NMR chemical shifts.

cis-VO_2^+ species at –485 ± 5 ppm is observed in acidic dmf solution which is necessary for the generation of the oxoperoxo ($VO(O_2)^+$) and oxodiperoxo species ($VO(O_2)_2^-$). A working mechanism for bromination is shown scheme 2.

(f) *Catalytic nature:* Under similar experimental conditions (ratio of substrate:V-complex:H_2O_2, 45:1:20), complex **2** takes 6 min for brominating xylene cyanole while a progressive decrease as a function of time is noticed in the absorbance. Further, the complex regains its original intensity in about 5–10 min. The increase in absorbance is due to the formation of an equilibrium mixture of Br_2, Br_3^- and OBr^-.

When **1** and **6** were treated with a ten-fold excess of H_2O_2 in dmf, the spectra showed bands at 400 and 312 nm. Addition of Et_4NBr to this mixture led to a marginal increase in the intensity of the 400 nm band. However on addition of 10 μl of 0·01 M HCl or 0·01 M $HClO_4$, the intensity of this band increases tremendously. Surprisingly both the complexes when treated with a ten-fold excess of KOH in dmf gave similar spectra with isosbestic points at 300, 334 and 392 nm over a period of 45–60 min. A new band at 315 nm persists. Addition of ten-fold excess of H_2O_2 showed similar isosbestic points at 300, 330 and 395 nm in both the complexes, indicating an equilibrium mixture of the complex and the free Schiff base in solution. Addition of KBr did not alter the spectra. However, addition of 0·1 M $HClO_4$ to the above mixture containing the complex, KOH, H_2O_2 and KBr led to a rapid increase in the intensity of the band at 400 nm. It has been shown that H_2O_2 can oxidize bromide under nearly neutral or acidic conditions[9–11], $H_2O_2 + Br^-$ + substrate → Br-Sub + H_2O + OH^-. Accumulation of OH^- prevents bromide oxidation and hence needs to be neutralized by excess acid. After sufficient equilibration of the complexes in $HClO_4$-dmf (10–30 min), the bromination of xylene cyanole was monitored by following the decrease in the intensity of absorption band at 615 nm for over a period of 120 min for **1–5** and **7–9**, and 6 min for complex **6** (figure 3). A control experiment performed without the vanadium complex and/or H_2O_2 or only in the presence of the Schiff base ligand, *H_2salamp*, showed some initial bromination activity of xylene cyanole, but the reaction did not proceed further. The bromination of phenol red was monitored by the disappearance of the band at 433 nm and appearance of a new band at 593 nm (inset, figure 3).

Complexes **1**, **3–9** take 120 min to show brominating activity to the same extent. However, the bromination of phenol red is faster and is completed within 3 min in case of complex **2**, while complexes **1**, **3–9** take 30 min for the same activity. Thus the brominating capacity, while on one hand substrate specific, on the other it also depends upon the stability of vanadium complex. The yield of the brominated products is ~70% based on the UV-VIS studies. Based on the V-complex to the substrate ratio of 1:45, it can be proposed that these reactions are catalytic in nature, with the turnover of **2** being 20 times more than that of **1**, **3–9**. In contrast to V-BrPO, which, functions optimally at approximately neutral *p*H, VO_2^+ functions only in acidic medium and at a rate $\approx 10^4$ times slower than V-BrPO. The turnover rate for V-BrPO under optimum bromide and H_2O_2 concentrations at *p*H 6·5 is $4{\cdot}7 \times 10^5$ mol of Br product/(mol enzyme) hr^{-1} whereas the turnover rate for bromination of xylene cyanole by various vanadium complexes reported here, **1**, **3–9**, is 15·75 mol Br product/(mol V) hr^{-1} and that of **6** is 315 Br produce/(mol V) hr^{-1} in 0·05 M $HClO_4$-dmf. Thus clearly the protein mediates the rapid peroxidative halogenation reaction at near-neutral *p*H. Mo(VI) and W(VI) mediated biomimetic chemistry of V-BrPO is also recently reported by Meister and Butler [12]. The turnover rate of MoO_3 catalysed bromination of 1,3,5-trimethoxybenzene is $\approx$ 180 Br product/(mol Mo) hr^{-1}, which is faster than VO_2^+ under the same conditions [11].

Acknowledgements

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References

1. (a) Asgedom G, Sreedhara A, Kivikoski J, Valkonen J, Kolehmainen and Rao C P 1996 *Inorg. Chem.* **35** 5674 (b) Rao C P, Sreedhara A, Rao P V, Verghese B M, Rissanen K, Kolehmainen E, Lokanath, N K, Sridhar M A and Prasad J S 1998 *J. Chem. Soc., Dalton Trans.* 2383
2. (a) Carrano C J, Nunn C M, Quan R, Bonalides J A and Pecoraro V L *Inorg. Chem.* 1990 **29** 944 (b) Li X, Lah M S and Pecoraro V L 1988 *Inorg. Chem.* **27** 4657
3. (a) Arber J M, De Boer E, Garner C D, Hasnain S S and Wever R 1989 *Biochemistry* **28** 7968 (b) Schindelin H, Kisker C, Hilton J, Rajagopalan K V and Rees D C *Science* **272** 1615 (c) McAlpine A S, McEwan A G and Bailey S 1998 *J. Mol. Biol.* **275** 613
4. Asgedom G, Sreedhara A, Kivikoski J, Valkonen J and Rao C P 1995 *J. Chem. Soc., Dalton Trans.* 2459
5. Asgedom G, Sreedhara A, Rao C P and Kolehmainen E 1996 *Polyhedron* **15** 3731
6. Asgedom G, Sreedhara A, Kivikoski J and Rao C P 1997 *Polyhedron* **16** 643
7. Rao C P, Sreedhara A, Rao P V, Lokanath N K, Sridhar M A, Prasad J S and Rissanen K 1999 *Polyhedron* **18** 289
8. Asgedom G, Sreedhara A, Kivikoski J, Kolehmainen E and Rao C P 1996 *J. Chem. Soc., Dalton Trans.* 93
9. Clague M J, Keder N L and Butler A 1993 *Inorg. Chem.* **32** 4754
10. Golpas G J, Hamstra B J, Kampf J W and Pecoraro V L 1994 *J. Am. Chem. Soc.* **116** 3627
11. Colpas G J, Hamstra B J, Kampf J W and Pecoraro V L 1996 *J. Am. Chem. Soc.* **118** 3469
12. Meister G E and Butler A 1994 *Inorg. Chem.* **33** 3269