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NMR and theoretical study on interactions between diperoxovanadate complex and 4-substituted pyridines

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Abstract

To understand the substituting group effects of organic ligands on the reaction equilibrium, the interactions between diperoxovanadate complex $[OV(O_2)_2(D_2O)]^-$/$[OV(O_2)_2(HOD)]^-$ and a series of 4-substituted pyridines in solution were explored using multinuclear (^1H, ^{13}C, and ^{51}V) magnetic resonance, DOSY, and variable temperature NMR in 0.15 mol/L NaCl ionic medium for mimicking the physiological condition. Some direct NMR data are given for the first time. The reactivity among the 4-substituted pyridines is pyridine > isonicotinate > *N*-methyl isonicotinamide > methyl isonicotinate. The competitive coordination results in the formation of a series of new six-coordinated peroxovanadate species $[OV(O_2)_2L]^{n-}$ (L = 4-substituted pyridines, $n = 1$ or 2). The results of density functional calculations provide a reasonable explanation on the relative reactivity of the 4-substituted pyridines. Solvation effects play an important role in these reactions.

Keywords: Diperoxovanadate; 4-Substituted pyridine; Interaction; NMR; Theoretical calculation

1. Introduction

Peroxovanadate complexes play an important role in the biosphere and are receiving renewed attention recently as a new kind of powerful insulin mimic or anticancer agents based on their biological response both *in vitro* and *in vivo* that may be developed into new oral drugs for anti-diabetes or tumor suppression [1–7]. However, the biochemical response mechanism of vanadium is very complex due to the numerous different possible ways vanadium can complex under physiological conditions. It is therefore not surprising to see that coordination chemistry and biological mechanism of vanadium compounds have recently stimulated much interest. For example, the Orvig [8,9] and Posner [10] groups have synthesized and characterized many vanadium complexes and studied their insulinomimetic activities *in vitro* or *in vivo*. Crans and co-workers have studied various vanadium compounds and reported that the coordination chemistry of vanadium has great versatility for adjustment of pharmacological characteristics [11,12]. Detailed and thorough potentiometric and ^{51}V NMR spectroscopic investigations of $H^+/H_2VO_4^-/H_2O_2$/Ligand systems have been performed by Pettersson and co-workers [13,14]. They also proposed a model describing the distribution of pentavalent vanadium in human blood based on speciation studies performed in the physiological medium of 0.15 mol/L NaCl with various blood constituents [15]. Conte and co-workers [16,17] have studied the NH_4VO_3/H_2O_2/histidine-like ligand systems that imitate the active site of haloperoxidases by using the electrospray ionization-mass spectrometry (ESI-MS), ^{51}V NMR, and density functional calculations. In our previous works [18–23], we have performed experimental and theoretical studies on the reactions of diperoxovanadate and a series of organic ligands in solutions. Especially, we explored how the substituting groups of picoline-like ligands affect the reaction equilibrium in the interaction systems in detail.

In this work, we used multinuclear (^1H, ^{13}C, and ^{51}V) magnetic resonance, DOSY, and variable temperature NMR to study the interaction systems NH_4VO_3/H_2O_2/L (L = 4-substituted

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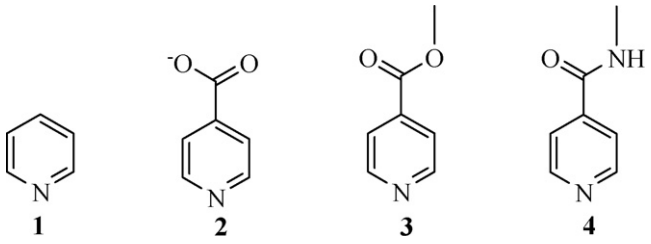


Scheme 1. Structural formula of pyridine (**1**), isonicotinate (**2**), methyl isonicotinate (**3**), and *N*-methyl isonicotinamide (**4**).

pyridines) in 0.15 mol/L NaCl ionic medium to probe the substituting group effects of organic ligands on the reaction equilibrium. Theoretical calculations are performed to provided a reasonable explanation on the experimental observations. Through the combined use of these methods, solution structures and coordination fashion of all species in the interaction systems can be determined and a better understanding of experimental phenomena can be achieved.

2. Experimental

2.1. Materials and preparations

The compounds D_2O, H_2O_2 (30%), NaCl, NaOH, NH_4VO_3, pyridine (abbr. Py, **1**), and isonicotinate acid, were commercial products (Sinopharm Chemical Reagent Company) used without further purification. The isonicotinate (abbr. *i*-nic, **2**) can be obtained by mixing the NaOH and isonicotinate acid with 1:1 molar ratio online. The ligands, methyl isonicotinate (abbr. Me-*i*-nic, **3**) and *N*-methyl isonicotinamide (abbr. *N*-Me-*i*-nicamide, **4**), were synthesized according to the literature [18] (Scheme 1). The ionic medium was chosen to represent the physiological condition, 0.15 mol/L NaCl D_2O solution at 20 °C in all NMR experiments except for the variable temperature NMR.

To form the ternary $NH_4VO_3/H_2O_2/L$ (L = **1**, **2**, **3**, and **4**) systems, NH_4VO_3 and H_2O_2 were first mixed in D_2O to produce the species $[OV(O_2)_2(D_2O)]^-/[OV(O_2)_2(HOD)]^-$ (abbr. bpV), then the ligands were separately added to the solution.

2.2. Spectroscopies

All spectra were recorded on Varian Unity plus 500 MHz NMR spectrometer, operating at 500.4 MHz for ^{1}H, 125.7 MHz for ^{13}C, and 131.4 MHz for ^{51}V NMR. DSS (3-(trimethylsilyl)-propanesulfonic acid sodium salt) was used as an internal reference for ^{1}H and ^{13}C chemical shifts. ^{51}V chemical shifts were measured relative to the external standard $VOCl_3$ with upfield shift being considered as negative. Signal-to-noise ratios were improved by a line-broadening factor of 2 or 10 Hz in the Fourier transformation of all ^{13}C or ^{51}V spectra.

DOSY spectra were recorded by using a *z*-gradient probe, which delivers a maximum gradient strength of 30 G/cm. The gradient compensated stimulated echo spin lock (GCSTESL) [24] was used to acquire DOSY spectra. The typical experimental parameters for a DOSY spectrum were as follows: gradient duration $\delta = 2.0$ ms, gradient strength $G = 30$ G/cm, spin lock time $\tau_{SL} = 1.0$ ms and time interval $\tau = 2.0$ ms. Diffusion coefficient was generally achieved by stepwise ramping up of the amplitudes of pulsed field gradients (PFGs), and diffusion times were optimized for every experiment. Reference deconvolution and baseline correction were adopted to compensate experimental imperfections.

2.3. Computational method

The geometries of the newly formed complexes were optimized using the B3LYP hybrid density functional, which includes a mixture of Hartree-Fock exchange with Beck88 exchange functional under generalized gradient approximation plus a mixture of Vosko–Wilk–Nusair local correlation functional and Lee–Yang–Parr non-local correlation functional [25–27]. The Wadt and Hay core-valence effective core potential [28] was used for the metal center (13 explicit electrons for neutral V) with the valence double zeta contraction of the basis functions (denoted as Lanl2dz in Gaussian [29]). For O, N, C, and H, the standard 6–31 + G* basis sets developed by Hariharan and Pople were used [30]. The single point solvation energy was calculated using Polarizable Continuum Models (PCM [31,32]) at each optimized gas phase geometry. Vibrational frequencies were calculated to ensure that each minimum is a true local minimum (only real frequencies). All calculations were carried out with the Gaussian 03 program suite [29].

3. Results and discussion

3.1. ^{51}V NMR of the interaction system of NH_4VO_3/H_2O_2/Ligands

The mixture of NH_4VO_3 and H_2O_2 with 1:5 molar ratio (0.2 mol/L vanadate concentration) has a ^{51}V peak locating at −692 ppm (Fig. 1), which is assigned to bpV according to previous reports [18–23]. When pyridine is added to bpV solution, a new single peak appears at about −711 ppm, which is assigned to the species $[OV(O_2)_2(Py)]^-$. Its intensity increases with the increasing of the quantity of pyridine (from 0.5 to 1.0, 2.0, and finally 3.0 equiv.) before reaching a maximum, as shown in Fig. 1. Moreover, with the addition of pyridine, the peak at −692 ppm slightly moves toward high field, whereas the peak at −711 ppm hardly moves. These may result from the change of pH value [22]. When the molar ratio between Py and bpV reaches 2:1, almost all bpV is converted to $[OV(O_2)_2(Py)]^-$.

Analogously, when 1.0 equiv. of a 4-substituted pyridine is added to the peroxovanadate solution, the area of bpV peak decreases and a new peak appears at about −710 ppm for isonicotinate {assigned to $[OV(O_2)_2(i\text{-nic})]^{2-}$}, −703 ppm for methyl isonicotinate {assigned to $[OV(O_2)_2(\text{Me-}i\text{-nic})]^-$}, and −705 ppm for *N*-methyl isonicotinamide {assigned to $[OV(O_2)_2(N\text{-Me-}i\text{-nic})]^-$}, as shown in Fig. 2. With the increase of ligand quantity, the area of new ^{51}V peak increases. From the

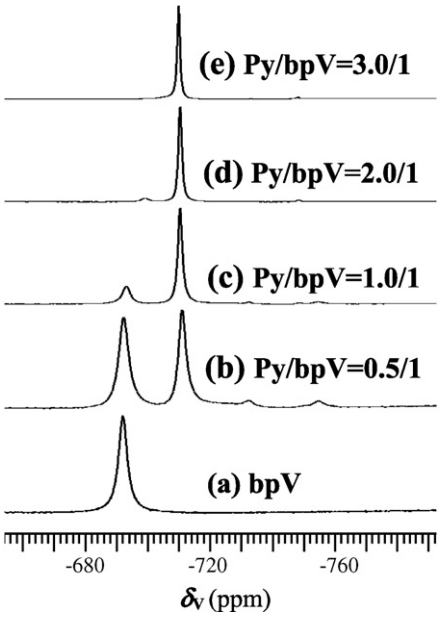


Fig. 1. ^{51}V NMR spectra of the interaction systems of bpV and Py, (a)–(e) corresponding to the molar ratios of Py/bpV = 0, 0.5, 1.0, 2.0, and 3.0, respectively. The total concentration of vanadate species is 0.2 mol/L.

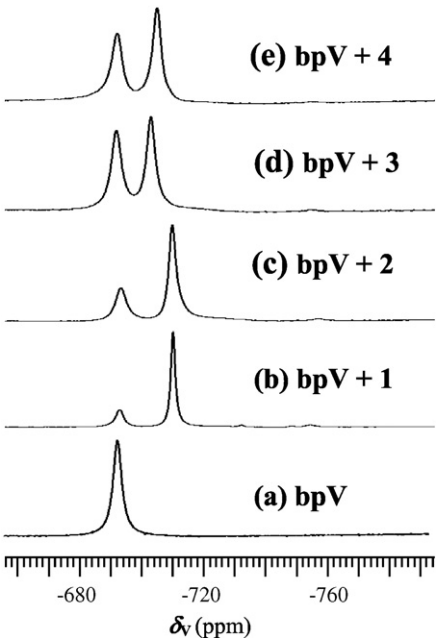


Fig. 2. ^{51}V NMR spectra of the interaction systems of NH_4VO_3/H_2O_2/4-substituted pyridine with 1:5:1 molar ratio in aqueous solution.

ratio of bpV peak areas before and after reaction, the order of interaction strength of 4-substituted pyridines with diperoxovanadate is deduced to be pyridine > isonicotinate > *N*-methyl isonicotinamide > methyl isonicotinate.

Variable temperature ^{51}V NMR was employed to study the influence of temperature on the equilibrium of the systems. As examples, the ^{51}V NMR spectra of the mixture of NH_4VO_3/H_2O_2/Me-*i*-nic and NH_4VO_3/H_2O_2/*i*-nic with 1:5:1 molar ratio and 0.2 mol/L vanadate concentration in the temperature range of 20–50 °C is shown in Fig. 3. It can be found from the experimental results that: (1) the quantity of the newly formed species decreases and all the peaks in the spectra move towards low field when the temperature is increased. This implies that with the increase of temperature, the bonds between vanadium and isonicotinate are weakened and the species is converted to bpV little by little. The chemical shift of bpV moves about 3.3 ppm every 10 °C, and the chemical shift of $[OV(O_2)_2$(Me-*i*-nic)$]^-$ moves about 1.9 ppm every 10 °C, shown in Fig. 3(A); (2) for different ligand, the thermal stability of the newly formed species is different. For example, about 25% $[OV(O_2)_2$(Me-*i*-nic)$]^-$ formed at 20 °C is converted to bpV at 50 °C, while the conversion efficiency of $[OV(O_2)_2(i\text{-nic})]^{2-}$ is only 5.7%, shown in Fig. 3(B). Therefore, the order of thermal stability is $[OV(O_2)_2(i\text{-nic})]^{2-} > [OV(O_2)_2$(Me-*i*-nic)$]^-$, in agreement with the variation of interaction strength between diperoxovanadate and the ligand; (3) the equilibrium is reversed when the temperature decreases, as reflected from the behaviors of the peaks in the spectra. The relative peak areas only depend on the

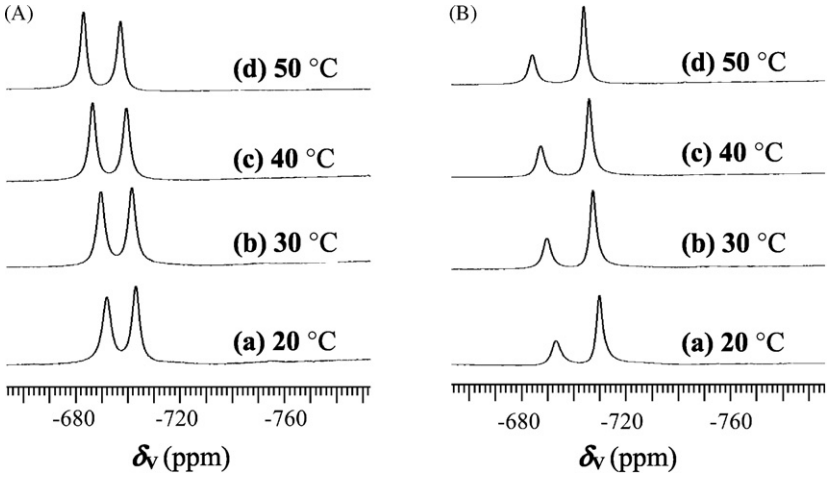


Fig. 3. Variable temperature ^{51}V NMR spectra of the interaction systems of NH_4VO_3/H_2O_2/Me-*i*-nic (A) and NH_4VO_3/H_2O_2/*i*-nic (B) with 1:5:1 molar ratio in aqueous solution.

Table 1
^{1}H and ^{13}C NMR spectral data of the interaction systems of diperoxovanadate and 4-substituted pyridines (molar ratio 1:1)

Systems	Species	Chemical shifts	
		^{1}H (ppm)	^{13}C (ppm)
bpV + Py	$[OV(O_2)_2(Py)]^-$	7.79 (s, 2H, Py–**H**), 8.22 (s, 1H, Py–**H**), 8.85 (s, 2H, Py–**H**)	152.1, 143.8, 129.0
	Py	7.61 (s, 2H, Py–**H**), 8.06 (s, 1H, Py–**H**), 8.60 (s, 2H, Py–**H**)	149.7, 142.2, 127.7
bpV + *i*-nic	$[OV(O_2)_2(i\text{-nic})]^{2-}$	8.06 (s, 2H, Py–**H**), 8.95 (s, 2H, Py–**H**)	174.3, 152.8, 151.0, 127.6
	i-nic	7.94 (s, 2H, Py–**H**), 8.71 (s, 2H, Py–**H**)	174.7, 150.5, 149.5, 126.6
bpV + Me-*i*-nic	$[OV(O_2)_2(\text{Me-}i\text{-nic})]^-$	4.03 (s, 3H, C**H**$_3$), 8.21 (s, 2H, Py–**H**), 9.02 (s, 2H, Py–**H**)	168.6, 153.4, 143.5, 128.0, 56.3
	Me-*i*-nic	4.00 (s, 3H, C**H**$_3$), 7.89 (s, 2H, Py–**H**), 8.69 (s, 2H, Py–**H**)	169.8, 152.1, 140.8, 126.1, 56.0
bpV + *N*-Me-*i*-nic	$[OV(O_2)_2(N\text{-Me-}i\text{-nic})]^-$	2.99 (s, 3H, C**H**$_3$), 8.02 (s, 2H, Py–**H**), 9.00 (s, 2H, Py–**H**)	169.8, 153.1, 147.6, 126.3, 29.2
	N-Me-*i*-nic	2.99 (s, 3H, C**H**$_3$), 7.70 (s, 2H, Py–**H**), 8.67 (s, 2H, Py–**H**)	171.2, 152.0, 144.7, 124.3, 29.3

temperature; and (4) the newly formed species is stable within the experimental temperature range.

3.2. ^{1}H and ^{13}C NMR data of the interaction systems

The ^{1}H and ^{13}C NMR spectral data of the interaction systems of bpV (0.2 mol/L) and 4-substituted pyridines with 1:1 molar ratio in sodium chloride deuterium oxide solution are listed in Table 1. There are two groups of 4-substituted pyridine peaks in each ^{1}H and ^{13}C NMR spectra, respectively. One group was assigned to the free 4-substituted pyridine and the other to the coordinated 4-substituted pyridine, *i.e.*, the ligand of the new species formed in the interaction system. According to the chemical shifts and the relative areas of the ^{1}H and ^{13}C peaks, we suggest that the newly formed species $[OV(O_2)_2L]^-$ is seven-coordinated.

3.3. DOSY spectra of the interaction systems

Different molecules have different self-diffusion coefficients while different groups in a molecule have almost the same self-diffusion coefficients. Therefore, we can use DOSY spectra to identify the components and their corresponding structures of the interaction systems. The DOSY spectra of $NH_4VO_3/H_2O_2/i$-nic and NH_4VO_3/H_2O_2/Me-*i*-nic in solution are shown in Fig. 4(A) and (B), respectively. There are two components containing proton except for the solvent. The component with slower diffusion rate marked by a dash line was assigned to the newly formed species $[OV(O_2)_2(i\text{-nic})]^{2-}$ or $[OV(O_2)_2(\text{Me-}i\text{-nic})]^-$. The component marked by a solid line was assigned to the free ligand. Therefore, the results of DOSY experiments support the 1D spectroscopic assignments mentioned above.

3.4. Theoretical study on the reaction products

The structures of the newly formed species were optimized using the B3LYP method. The results confirm above analysis that the newly formed species $[OV(O_2)_2L]^-$ (L = 4-substituted pyridines) are six-coordinated. The structure has an oxygen atom at the apex and the N atom in pyridine ring with the oxygen atoms of the peroxide groups at the equatorial plane. The V atom near the center of the pentagonal base and form a distorted pentagonal pyramid. The V–N bond length ranging from 2.20 to 2.23 Å for different 4-substituted pyridine, which are within the range of reported ones for diperoxovanadate complexes [19,20].

The reactivity of 4-substituted pyridine in solution depends on the intrinsic bonding strength between $[OV(O_2)_2]^-$ and L and the solvation effects. The free energies of the four reactions studied here are as follows:

$$\text{Py} + [OV(O_2)_2(H_2O)]^- \rightarrow [OV(O_2)_2(\text{Py})]^- + H_2O,$$
$$\Delta G\,(298\,\text{K}) = 2.35\,\text{kcal/mol (in gas phase) and}$$
$$-9.34\,kcal/mol\,(in\ solution) \quad (1)$$

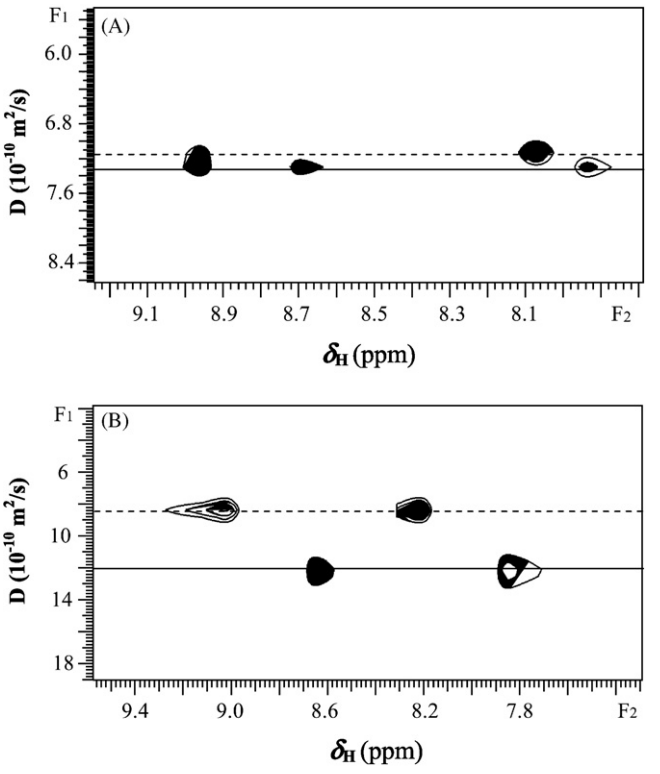
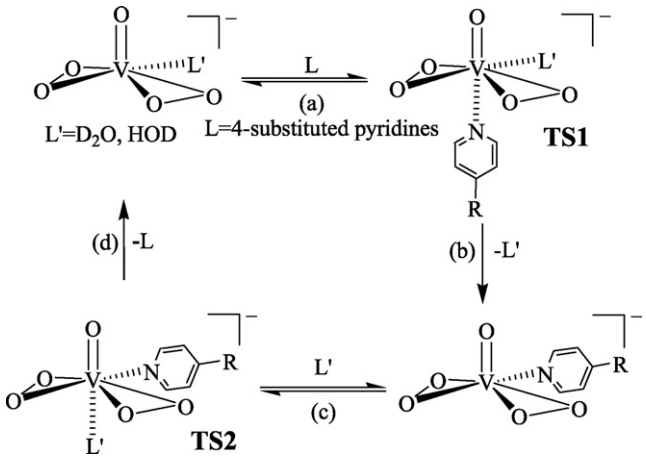


Fig. 4. DOSY spectra of the pyridine ring of the interaction systems of NH_4VO_3/H_2O_2/4-substituted pyridine (1:5:1) in aqueous solution. The 4-substituted pyridine is isonicotinate (A) or methyl isonicotinate (B). The peaks marked by a solid line are assigned to the free ligand. The peaks marked by a dash line are assigned to the coordinated ligand.



Scheme 2. Possible interaction modes between bpV and 4-substituted pyridines.

$$i\text{-nic} + [OV(O_2)_2(H_2O)]^- \rightarrow [OV(O_2)_2(i\text{-nic})]^{2-} + H_2O,$$
$$\Delta G\,(298\,K) = 38.2\,kcal/mol\ (in\ gas\ phase) and$$
$$-7.98\,kcal/mol\ (in\ solution) \quad (2)$$

$$Me\text{-}i\text{-nic} + [OV(O_2)_2(H_2O)]^- \rightarrow [OV(O_2)_2(Me\text{-}i\text{-nic})]^- + H_2O,$$
$$\Delta G\,(298\,K) = 3.15\,kcal/mol\ (in\ gas\ phase)\ and$$
$$-5.97\,kcal/mol\ (in\ solution) \quad (3)$$

$$N\text{-Me-}i\text{-nicamide} + [OV(O_2)_2(H_2O)]^- \rightarrow$$
$$[OV(O_2)_2(N\text{-Me-}i\text{-nicamide})]^- + H_2O,$$
$$\Delta G\,(298\,K) = 3.07\,kcal/mol\ (in\ gas\ phase)\ and$$
$$-6.21\,kcal/mol\ (in\ solution) \quad (4)$$

These indicate that the reactions are impossible in the gas phase but thermodynamically favorable in the solution. The free energy changes of these four reactions resulting from solvation effects are 11.69, 46.18, 9.28, and 9.12 kcal/mol, respectively. Obviously, solvation effects play an important role, especially for reaction (2). The large free energy variation for reaction (2) is due to the negative charged character of *i*-nic ligand. Comparison of the free energies of reactions (1)–(4) in solution shows that:

$$\Delta G\,(\text{reaction 1}) < \Delta G\,(\text{reaction 2}) < \Delta G\,(\text{reaction 4}) < \Delta G\,(\text{reaction 3})$$

This order is in agreement with the reactivity between 4-substituted pyridines and bpV observed experimentally.

3.5. Reaction modes of the interaction systems

After analyzing and comparing the ^1H, ^{13}C and ^{51}V NMR spectra of the interaction systems, we suggest the possible reaction modes as follows (see Scheme 2): (1) the 4-substituted pyridine (abbr. L) attacks the vanadium of bpV from the opposite site of the terminal oxygen and forms a seven-coordinated (pentagonal bipyramidal) transition state **TS1** (route a). Accompanied by the leaving of the water molecule, **TS1** turns into a six-coordinated species $[OV(O_2)_2L]^-$ (route b); (2) a similar process can occur between $[OV(O_2)_2L]^-$ and a water molecule and forms **TS2** (route c) and finally bpV (route d).

4. Conclusions

Several NMR experimental techniques were employed to study the interactions between diperoxovanadate complex and a series of 4-substituted pyridines in the 0.15 mol/L NaCl D_2O solution. The experimental results indicate that new six-coordinated peroxovanadate species is formed. The relative activity of these organic ligands is as follows: pyridine > isonicotinate > *N*-methyl isonicotinamide > methyl isonicotinate. Solvation effects play an important role in the reactions.

Acknowledgments

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