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Synthesis and Properties of μ-Oxo-bis(oxo-peroxo-6-(1-hydroxyalkyl)nicotinicacidvanadium(V) Complexes. C-6 Alkyl Substitution of Nicotinic Acid in Aqueous Peroxo Vanadium(V) Solutions

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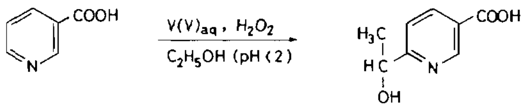
In a critical review [1] Di Furia and Modena concluded that no unified mechanism for oxygen transfer processes for transition metal complexes exists, and that some peroxo complexes may be initiators or carriers of radical reactions. Various intermediates, transition states and pathways are possible for different reactions, which thus may yield different products [2]. The work reported here represents an excellent illustration for such a situation. We have characterized the products of an unusual reaction, but are baffled by the diversity of intermediates and transition states one can imagine to exist in the course of this reaction. We report here the experimental facts, leaving open the intriguing question of the mechanism of this process.

A crystalline red compound of the formula $[O\{VO(O_2)(C_8H_9NO_3)\}_2]$ was obtained from the aqueous vanadium(V) peroxide solutions containing nicotinic acid, by precipitating with ethanol. The compound was insoluble in water and most organic solvents, but soluble in DMSO and DMF. According to the analysis, it contained an ethanol unit in addition to one mole of nicotinic acid per vanadium. It was quickly determined that alcohol is not simply a part of the crystal lattice, and that an ethoxy group was somewhere firmly bound. Initially, the amount of the red compound obtained was very small. After numerous experiments a modified procedure** increased the yield to 20–25%, enabling further characterization of the compound. ^1H and ^{13}C NMR, supported by IR spectra, revealed that the ethylester of nicotinic acid which is a plausible product, is not present in the complex. The spectral evidence indicated that a startling C-6 substitution of the nicotinic acid by a C-1 hydroxyethyl group has occurred. Such formation of a carbon–carbon bond in an aqueous solution under these mild conditions ($pH < 2$) as shown below, is unusual, and this unexpected substitution was confirmed by additional independent experiments. The red complex was hydrolyzed by conc. KOH, the solution was neutralized (4 M HCl), and then continuously extracted by CH_2Cl_2 over a period of 48 h, rendering a colorless product. In a separate experiment, the 6-(1-hydroxyethyl)nicotinic acid was prepared via a photochemical addition reported in the literature [3]. ^1H and ^{13}C NMR spectra of the three compounds: the vanadium complex, the ligand extracted from the hydrolyzed complex solution, and the photochemically synthesized 6-(1-hydroxyethyl)nicotinic acid were then run in DMSO-d_6, giving reproducible spectra. The proton and ^{13}C resonances observed for these substances were compared and, as shown in Table I, the ^1H spectra of the extracted ligand and the synthesized compound are practically identical, proving that the C-6 substitution by 1-hydroxyethyl group has indeed occurred.



nicotinic acid 6-(1-hydroxyethyl)nicotinic acid

^1H NMR of the red vanadium complex in DMSO-d_6 provided the primary source of evidence according to which the compound was identified by the following features. Integration yielded a 1:1:1 ratio for the signals in the aromatic region, and a 1:3 ratio for the aliphatic signals, showing that an aromatic proton signal pattern of nicotinic acid was missing. The chemical shifts of the remaining three aromatic protons were considerably different from those observed in nicotinic acid [4], however the coupling constants of the ring protons were unchanged, with one important exception: the *ortho* coupling J(5-6) of 5 Hz and one of the *meta* couplings, J(4-6) of 2 Hz, were missing. The coupling pattern and the

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**See right-hand column for footnote.

**Preparation of $[O\{VO(O_2)(C_8H_9NO_3)\}_2]$. V_2O_5 (0.91 g) was dissolved in water (10 ml) containing KOH (0.92 g) at 50 °C. The clear filtered solution was cooled and H_2O_2 (30%, 5 ml) was gradually added under stirring in an ice bath, followed by nicotinic acid (2.46 g). The solution was left stirring in the ice bath for an hour, after which cold ethanol (95%, 5 ml) was added. To this ice cooled solution H_2SO_4 (0.5 M, 72 ml) was added over a period of 20 min, followed by ethanol (95%, 10 ml). The stirring of the cooled deep-burgundy colored solution was continued for about 2 min. The ice bath was then allowed to warm up slowly to room temperature, and after 20–30 min gas evolution started. Three to seven hours later a red crystalline precipitate formed, which had to be filtered off to prevent dissolution. The uniform scallop shaped microcrystals were washed with cold water and ethanol. Calc. for $C_8H_9NO_{6.5}V$: C, 35.0; H, 3.3; N, 5.1; O_2^{2-}, 11.7; V, 18.5. Found: C, 36.2; H, 3.4; N, 5.3; O_2^{2-}, 11.1; V, 17.7%. The increased H_2SO_4 concentration increases the rate of the reaction, and the precipitation and dissolution of red crystals may be missed. Successful preparations have been achieved with 0.5, 1.0 and 2 M H_2SO_4.

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TABLE I. ^1H NMR Spectral Data and Assignments in DMSO-d_6. δ(TMS) = 0.00 ppm

Peak assignment[a]	Chemical shift			
	$O\{VO(O_2)(C_8H_9NO_3)\}_2$	extracted ligand	6-(1-hydroxyethyl)nicotinic acid	
			prepared by photosynthesis	literature data [3]
H(2)	9.93	8.96	8.98	9.00
H(4)	8.69	8.26	8.28	8.19
H(5)	8.11	7.64	7.65	7.42
$-\overset{\mathrm{OH}}{\overset{\vert}{\mathit{C}}}\mathit{H}-\mathrm{CH_3}$	6.61	4.79	4.80	4.82
$-\overset{\mathrm{OH}}{\overset{\vert}{\mathrm{C}}}\mathrm{H}-\mathit{CH_3}$	2.04	1.38	1.39	1.43

[a]The aromatic protons are numbered according to the numbering scheme of the carbon atoms to which they are bound, and aliphatic protons are in italics.

coupling constants observed for the aromatic protons in the spectrum of the vanadium complex therefore clearly indicated that the C-6 proton was missing. Aliphatic protons showed a doublet for the methyl group, implying that one of the methylene protons was absent. The presence of this doublet positively showed that the C-1 carbon of the alcohol was attached to the C-6 nicotinic acid, and the ^1H NMR hence ruled out the possibility of the nicotinic acid ester existence. Table I shows that the spectrum of the ligand, obtained by extraction of the hydrolyzed metal complex solution, and the spectrum of the 6-(1-hydroxyethyl)nicotinic acid obtained by photosynthesis are practically identical. In the red vanadium complex all the ^1H resonances are shifted with respect to the free ligand, as expected for a coordinated organic molecule. The largest deshielding is observed for the methine protons, indicating the oxygen coordination to the metal. The next largest significant shift of H(2) reflects a change in the nitrogen environment, implying under the circumstances the nitrogen coordination to vanadium. The ^{13}C NMR spectra were obtained for the potassium salt of the hydrolyzed ligand (formed by KOH hydrolysis of the compound in water) and the potassium salt of the 6-(1-hydroxyethyl)nicotinic acid obtained in the course of the photosynthesis. The chemical shifts of the two are practically identical (23.9; 70.9; 120.5; 131.6; 139.3; 149.4; 167.4 and 174.2 ppm), providing a further confirmation for the proposed substitution.

The IR spectrum of the red vanadium complex contributed additional information for its structure. The very strong band at 1707 cm^{-1} is typical for the ν_{as}(COO) of a protonated carboxylato group [5]. ν_s(COO) occurs at 1423 cm^{-1}, and the difference of 284 cm^{-1} between the two also indicates the presence of a protonated, free or monodentately coordinated carboxylate [6]. The ν(V=O) and ν(O–O) occur as very strong, sharp bands at 995 and 934 cm^{-1}, respectively; both at a rather high frequency, observed for monoperoxovanadates [7, 8]. In the lower energy region, well resolved bands present between 395–375 cm^{-1} and at 340 cm^{-1} most likely represent (V–O) and (V–N) stretchings, respectively [9].

The electronic absorption spectrum of the red complex in the solid state (Nujoll mull) and solutions shows two characteristic absorptions: the strong $\pi-\pi^*$ band [10] at 270 nm (Nujol) and 266 nm in DMSO (ϵ ~12 000 l cm^{-1} mol^{-1}), and the weak LMCT [8, 11] bands observed in Nujol at 435 nm, and at 430 and 408 nm in DMSO and DMF, respectively, with an expected low molar absorptivity of about 400 l cm^{-1} mol^{-1}.

The synthesis of analogous V(V) complexes with different alcohols has so far been successful with n-propanol. Pale orange prismatic crystals do not appear to be isomorphous with the ethyl derivative, but have similar properties and are also too small for an X-ray analysis. Chemical analysis, ^1H and ^{13}C NMR spectra, agree with the expected composition $O\{VO(O_2)(C_9H_{11}NO_3)\}_2$ involving the C-6 substitution of nicotinic acid by the 1-hydroxy-n-propyl group. The IR spectrum of the complex displays typical features similar to the ethyl derivative, and the ^1H NMR spectrum shows the expected signal patterns for aromatic and aliphatic protons.

Figure 1 represents the simplest possible structure of these two red complexes involving a bidentate coordination of the organic ligand, indicated by ^1H NMR, and an oxo and a bidentately coordinated peroxo group, implied by IR spectra. The protonated carboxylate may or may not be engaged in an intermolecular bridging, which would raise the coordina-

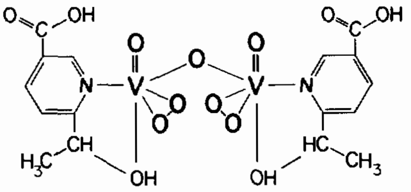

Fig. 1. Proposed molecular structure of $[O\{VO(O_2)(C_8H_9NO_3)\}_2]$.

tion number of V(V) to seven, and the OH group present are probably involved in strong hydrogen bonding. These compounds are very stable, and some samples left standing for over a year have not shown any loss of peroxides. The bidentate coordination of the 6-(1-hydroxyalkyl)nicotinic acid, forming a five-membered ring with vanadium, may well be a major factor contributing to the stability of the complex, which trapped the molecule into the V(V) peroxo heteroligand sphere. By precipitation of the insoluble red compounds the 6-(1-hydroxyalkyl)nicotinic acid was then separated from the aqueous solution, where a complicated chain of radical intermediates must have been involved in the burgundy red reaction mixture.

Recently we reported [12] the preparation and properties of V(V) and Mo(VI) oxodiperoxonicotinic acid complexes. We have not observed the C-6 substitution of nicotinic acid in analogous Mo(VI) peroxo systems. Another unusual V(V) catalyzed oxidation of 2,2′-bipyridine to pyridine-2-carboxylic acid was previously reported by Szentivanyi and Stromberg [13]. The late discovery of vanadium bromoperoxidases [14, 15] and vanadium nitrogenases [16, 17] increased the importance of V(V) peroxo heteroligand complexes. Notably, the region in the UV–Vis spectrum used for testing of the activity of vanadium peroxidases (412 and 460 nm [18]) overlaps with the wavelength where LMCT bands occur in monoperoxo heteroligand V(V) complexes [8]. These monoperoxo complexes deserve special attention, because they have proved to be more active as oxidation catalysts than the diperoxo heteroligand vanadates [1, 19].

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