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PHOTOREDOX BEHAVIOR OF TRI-μ-OXO-BIS[(5,10,15,20-TETRATOLYLPORPHINATO)NIOBIUM(V)][1)]

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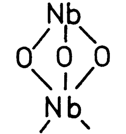
The tri-μ-oxo dimer of (5,10,15,20-tetratolylporphinato)niobium(V), $[Nb^{V}(ttp)]_2O_3$, was reduced upon irradiation with the visible light in benzene containing an alcohol under anaerobic conditions, while the irradiation of the complex in benzene afforded oxygenated radical complexes under aerobic conditions.

The redox chemistry of metalloporphyrins has attracted much attention in connection with the development of oxygen carriers, oxygenation catalysts, and photochemical catalysts. We have investigated the redox chemistry of some molybdenum[2)] and niobium[3)] complexes of 5,10,15,20-tetraphenylporphine by means of electrochemical methods. The redox potentials for couples of Mo^{V}/Mo^{IV} and Nb^{V}/Nb^{IV} as observed for these molybdenum and niobium porphyrins have been found to vary depending upon the nature of axial ligands, and fall in the region between 0 and -0.8 V vs. SCE. Ledon and his associates have reported that the photo-assisted reduction of molecular oxygen to hydrogen peroxide took place in the presence of the 5,10,15,20-tetraphenylporphinato complex of oxoethoxomolybdenum(V).[4)] We have recently clarified the mechanistic aspect of photoreduction of the oxoalkoxo(5,10,15,20-tetratolylporphinato)molybdenum(V) complexes, $Mo^{V}(O)(OR)(ttp)$: photochemical homolysis of the axial coordination bond, Mo-OR, is followed by diffusion of the generated radical species, RO·, out of the metal-coordination sphere.[5)] The latter process determines the overall reduction rate for the complexes with less polar axial ligands, while the former becomes the rate determining step for those with axial ligands of more polar character. We report here the redox behavior of the (5,10,-15,20-tetratolylporphinato)niobium(V) complexes upon irradiation with the visible light.

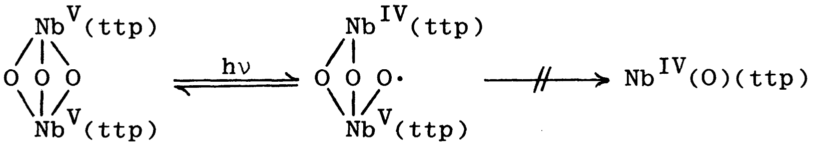
The tri-μ-oxo dimer of (5,10,15,20-tetratolylporphinato)niobium(V), $[Nb^{V}(ttp)]_2O_3$, was not reduced photochemically despite the fact that its reduction potential is less negative than those of the oxoalkoxomolybdenum(V) complexes, $Mo^{V}(O)(OR)(ttp)$, while the latter molybdenum complexes were readily reduced upon irradiation with the visible light in benzene (Eq. 1). Since there is no significant difference in energy demand for the homolytic metal-oxygen bond cleavage between oxomo-



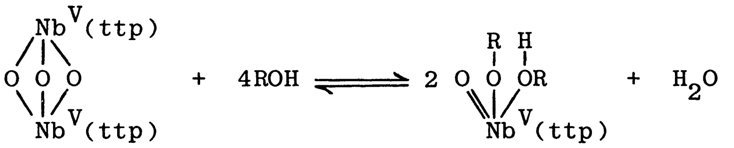
$[Nb^{V}(ttp)]_2O_3$

$$Mo^{V}(O)(OR)(ttp) \xrightarrow{h\nu} Mo^{IV}(O)(ttp) + RO\cdot \qquad (1)$$

lybdenum and oxoniobium complexes, the fast recombination of the photo-generated pair of the oxo radical and the niobium(IV) species seems to be responsible for the inhibition of the photoreduction of the niobium dimer (Eq. 2). The oxo radical can not diffuse out from the coordination sphere of the reduced niobium species because the two niobium atoms are linked with the residual oxo bridges.


(2)

As shown in Fig. 1, $[Nb^{V}(ttp)]_2O_3$ gives an ESR signal consisting of ten hyperfine lines upon irradiation with the visible light in benzene containing an alcohol species under anaerobic conditions. The ESR spectrum is identical with that observed for the oxo(5,10,15,20-tetraphenylporphinato)niobium(IV) complex obtained by chemical or electrochemical reduction;$^{3)}$ $\bar{g}$ and $\bar{A}$(Nb) values being 1.96 and 1.75 x 10^{-2} cm^{-1}, respectively. The observation is consistent with the formation of the monomer species via ligand exchange reaction (Eq. 3), followed by its reduction to the niobium(IV) complex.


(3)

An attempt to isolate the oxoalkoxoniobium(V) monomer complex was failed due to its fast hydrolysis followed by dehydration to give the tri-μ-oxo dimer. The Q and B bands appeared at 418 and 550 nm, respectively, for $[Nb^{V}(ttp)]_2O_3$ are shifted to longer and shorter wavelength regions, respectively, upon addition of 1-butanol (Fig. 2). The formation constants for the alkoxo complexes, based on Eq. 3, were evaluated by the spectrophotometric method with the three different alkoxo ligands

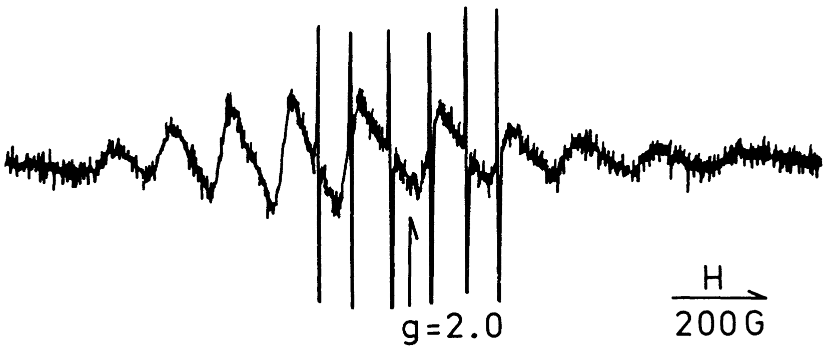


Fig. 1. ESR spectrum of $Nb^{IV}(O)(ttp)$ generated upon irradiation of $[Nb^{V}(ttp)]_2O_3$ with the visible light in benzene containing ethanol at room temperature under anaerobic conditions.

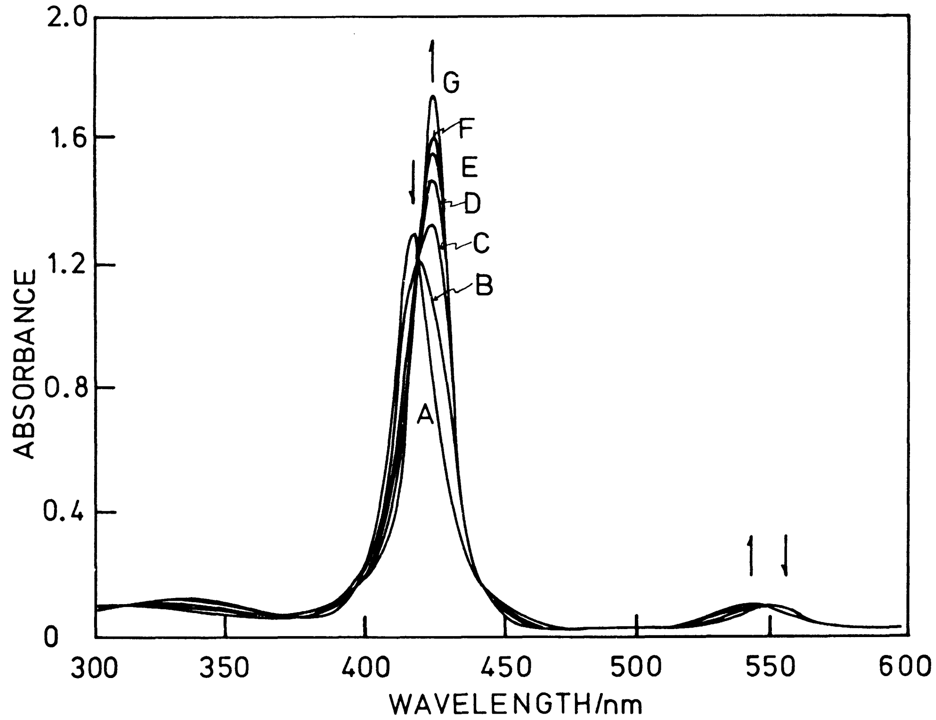


Fig. 2. Electronic spectral change observed for $[Nb^{V}(ttp)]_2O_3$ (2.93×10^{-6} mol dm^{-3}) in xylene at 23.0 °C upon addition of the following amounts of 1-butanol: A, none; B, 10; C, 20; D, 30; E, 40; F, 50; G, 100 µL to a 4.0-mL sample of the xylene solution of $[Nb^{V}(ttp)]_2O_3$. Trends of spectral change are shown by arrows.

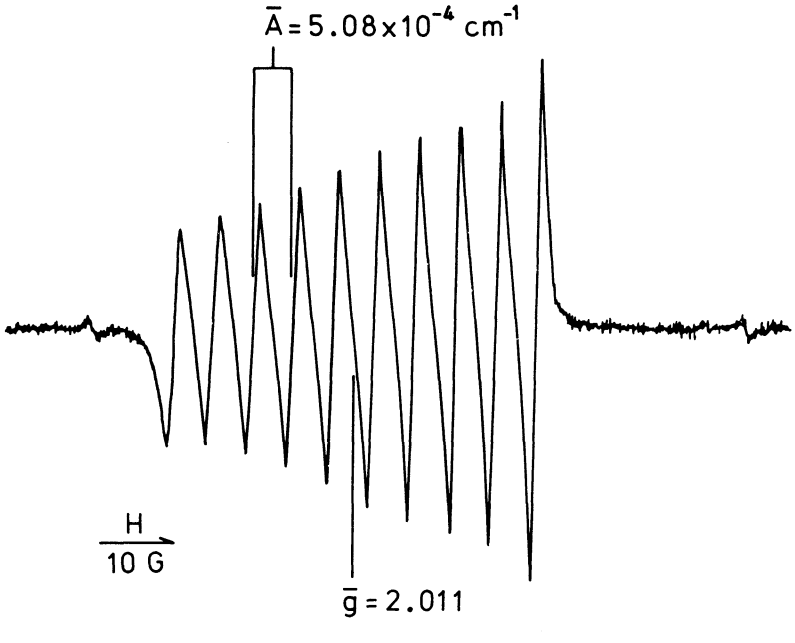
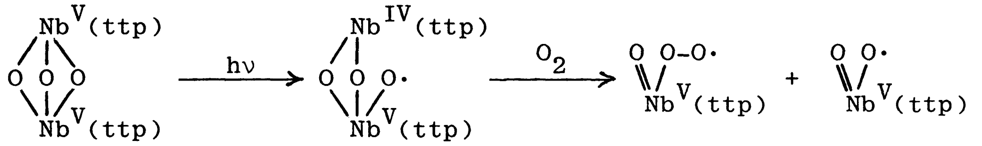


Fig. 3. ESR spectrum of $Nb^{V}(O)(OO\cdot)(ttp)$ generated upon irradiation of $[Nb^{V}(ttp)]_2O_3$ in benzene with the visible light at room temperature under aerobic conditions.

at 23.0 °C in xylene: ethoxo, 1.5 x 10^{-7}; 1-butoxo, 4.7 x 10^{-7}; benzyloxo, 3.2 x 10^{-6} mol^{-2} dm^{6}. The alkoxo radical species generated during the photoreduction process were detected by means of the spin trapping technique with nitrosobenzene as a trapping agent.

As shown in Fig. 3, $[Nb^{V}(ttp)]_2O_3$ in benzene gives an ESR signal consisting of ten hyperfine lines upon irradiation with the visible light under aerobic conditions; $\bar{g}$ and $\bar{A}$(Nb) values being 2.011 and 5.08 x 10^{-4} cm^{-1}, respectively. The intensity for these hyperfine lines increases as the resonance field is raised. This spectral feature strongly indicates that the paramagnetic species generated under aerobic conditions has some uniaxial or pseudo-uniaxial structure with respect to the location of an odd electron. The ESR signal rapidly vanished by the following treatments: addition of ethanol, interruption of the irradiation, and deoxygenation. On the basis of comparison of the $\bar{A}$(Nb) value for the complex obtained by the aerobic irradiation with that for the monomeric oxoniobium(IV) complex, the odd-electron population at the niobium nucleus for the former complex is 2.9% of that for the latter. This means that the odd electron is located primarily on the ligand portion for the former complex. The ESR signal retained its intensity without any detectable change under the aerobic irradiation conditions for more than several days, while either addition of a radical scavenger such as ethanol or interruption of the irradiation resulted in immediate quenching of the signal. In the light of the above observations, $[Nb^{V}(ttp)]_2O_3$ must undergo homolytic cleavage to give the niobium(IV) species and subsequently oxidized under the aerobic irradiation conditions to afford the paramagnetic species as shown by Eq. 4.



(4)

Recently, Richard and Guilard obtained similar dioxygen complexes by the reaction of niobium(IV) complexes of 5,10,15,20-tetraphenylporphine with molecular oxygen; the $\bar{A}$(Nb) value being somewhat larger than that observed here.$^{6)}$ Their oxygen adducts were reported to be stable at room temperature, while the radical species obtained in this work is highly reactive under comparable conditions. Since either or both of the paramagnetic complexes are considered to be strong oxidants, the present photochemical system is expected to be utilized to simulate the catalytic functions of cytochrome P-450. Our study is in progress along this line.

References

1) Contribution No. 758 from this Department.
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