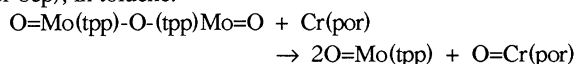


Oxygen Atom Transfers from μ -Oxo-bis(Oxomolybdenum(V) Porphyrin) to Chromium(II) Porphyrins in Toluene

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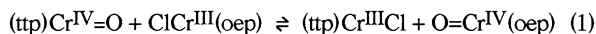
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Simple complete oxygen-atom transfers between metalloporphyrins mediated by two-electron pathways were observed quantitatively from μ -oxo-bis(oxomolybdenum(V) porphyrin), $[\text{MoO}(\text{tpp})]_2\text{O}$,¹ to chromium(II) porphyrins, $\text{Cr}(\text{por})$ (por = tpp or oep), in toluene.

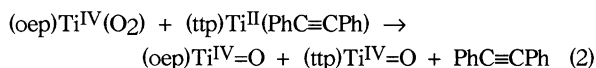


The presence of excess of $\text{Cr}^{\text{II}}(\text{por})$ yielded $[\text{Cr}^{\text{III}}(\text{por})]_2\text{O}$.

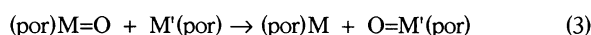
Although the study of oxygen atom transfer reactions is very substantial to clarify the reaction mechanisms of many metalloenzymes such as cytochrome P-450, xanthine oxidase, sulfite oxidase, and nitrate reductase, the oxygen atom transfer reactions between metal complexes are less common.^{2,3} Metalloporphyrins are well suited for the study of atom transfer reactions involving multi-electron pathways.⁴ As a typical example of complete (no formation of μ -oxo complexes) oxygen-atom transfer reactions mediated by one-electron process between metalloporphyrins, the reaction of eq 1 has been reported,⁵ which is accompanied by simultaneous Cl atom transfer.



Intriguing oxygen-atom transfer reactions were also reported for a system of titanium porphyrins which involves a two-electron reduction of peroxide (O_2^{2-}) to 2O^{2-} by $\text{Ti}(\text{II})$.^{2,6}



However, simple complete oxygen-atom transfers (two-electron process without dissociation of ligands and other atom transfers than an oxygen atom) between metalloporphyrins as shown in eq 3 have not been reported so far.²



The present work reports the first simple complete oxygen-atom transfers from $[\text{Mo}^{\text{VO}}(\text{tpp})]_2\text{O}$ to $\text{Cr}^{\text{II}}(\text{por})$ in toluene at 20°C.

Since $[\text{Mo}^{\text{VO}}(\text{tpp})]_2\text{O}$ is photosensitive⁷ and $\text{Cr}^{\text{II}}(\text{por})$ and $\text{Mo}^{\text{IV}}\text{O}(\text{tpp})$ which were treated as parent complexes and products are very unstable in aerated solutions, all solutions were prepared under scrupulously oxygen-free conditions. Reactants were treated separately in the vessels of a glass apparatus with optical cells or NMR tubes connected to a vacuum line and dissolved in toluene which was beforehand degassed strictly by freeze-evacuate-thaw cycles under 10^{-5} – 10^{-6} Torr (1 Torr = 133 Pa), followed by mixing of those reaction solutions by the break-seal method in the dark. It took at least 2 min to mix the two reactant solutions completely. All complexes used in this work were prepared and identified by UV-vis, IR, ^1H NMR, and ESR spectral methods.⁸

The complexes, $[\text{Mo}^{\text{VO}}(\text{tpp})]_2\text{O}$ and $\text{Cr}^{\text{II}}(\text{tpp})$, in toluene have the Soret bands at 445 nm ($\epsilon/10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1} = 12.0$) and 423 nm (31.5), respectively, as shown in Figure 1. When

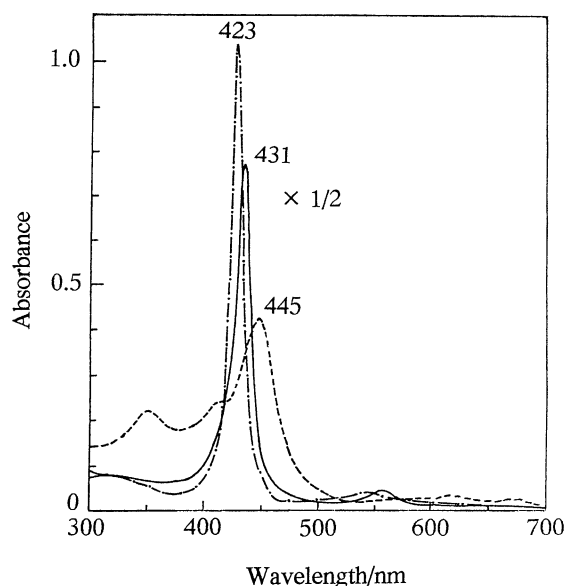
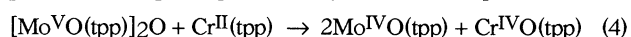


Figure 1. UV-vis spectra of $\text{Cr}^{\text{II}}(\text{tpp})$ (—, $3.5 \times 10^{-5} \text{ mol dm}^{-3}$), $[\text{Mo}^{\text{VO}}(\text{tpp})]_2\text{O}$ (---, $3.5 \times 10^{-5} \text{ mol dm}^{-3}$) in toluene, and the mixed solution containing the same amounts of the two porphyrin complexes (—) at 20°C.

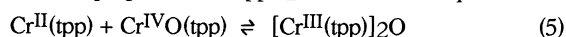
the two solutions with the same volume and concentration were mixed to give a solution (each concentration: $3.5 \times 10^{-5} \text{ mol dm}^{-3}$), the absorption bands due to the two complexes disappeared within the handling time of 2 min with simultaneous appearance of bands around 431 nm, which is consistent with the formation of $\text{Mo}^{\text{IV}}\text{O}(\text{tpp})$ (431 nm, $\epsilon/10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1} = 34.7$) and $\text{Cr}^{\text{IV}}\text{O}(\text{tpp})$ (432 nm, 21.6). Since the two expected products have overlapped spectra, direct quantitative analysis of the products are not possible. The quantitative formation of both complexes was confirmed however by introduction of moisturized air to the resulting solution, which caused spectral change by the formation of $\text{Mo}^{\text{VO}}(\text{tpp})\text{OH}$ (464 nm, 9.0)¹³ from the unstable product of $\text{Mo}^{\text{IV}}\text{O}(\text{tpp})$. The amount of $\text{Mo}^{\text{VO}}(\text{tpp})\text{OH}$ was estimated to be $\sim 7.0 \times 10^{-5} \text{ mol dm}^{-3}$, and then the concentration of the initial product $\text{Mo}^{\text{IV}}\text{O}(\text{tpp})$ should be $\sim 7.0 \times 10^{-5} \text{ mol dm}^{-3}$. The amount of $\text{Cr}^{\text{IV}}\text{O}(\text{tpp})$ was estimated by subtracting the spectrum of $\text{Mo}^{\text{IV}}\text{O}(\text{tpp})$, and was $\sim 3.5 \times 10^{-5} \text{ mol dm}^{-3}$. These UV-vis spectral analyses indicated that the oxygen atom transfer reaction mediated by two-electron pathways took place quantitatively as shown in eq 4.



Irreversibility of eq 4 was demonstrated by treatment of $\text{Cr}^{\text{IV}}\text{O}(\text{tpp})$ with $\text{Mo}^{\text{IV}}\text{O}(\text{tpp})$ as parent complexes in toluene, which caused no absorption spectral change. This result also

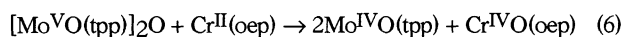
verified no formation of the μ -oxo mixed-metal complexes like (tpp)OMo-O-Cr(tpp) as final products.

When an excess of $\text{Cr}^{\text{II}}(\text{tpp})$ was used as a starting complex for the reaction with $[\text{Mo}^{\text{VO}}(\text{tpp})]_2\text{O}$, new bands at 414 and 542 nm appeared besides the bands around 431 and 552 nm. The new bands were in coincide with those of $[\text{Cr}^{\text{III}}(\text{tpp})]_2\text{O}$ reported by West et al.¹⁴ They observed the bands around 414 and 542 nm by mixing the solutions of $\text{Cr}^{\text{II}}(\text{tpp})$ and $\text{Cr}^{\text{IV}}\text{O}(\text{tpp})$, and concluded the formation of $[\text{Cr}^{\text{III}}(\text{tpp})]_2\text{O}$. In the present case, the reaction of an excess of $\text{Cr}^{\text{II}}(\text{tpp})$ with $\text{Cr}^{\text{IV}}\text{O}(\text{tpp})$ which was produced in eq 4 gave $[\text{Cr}^{\text{III}}(\text{tpp})]_2\text{O}$ as shown in eq 5.

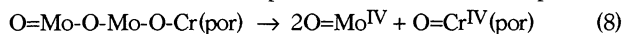
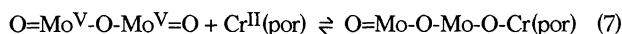


^1H NMR spectral measurements were tough works for the reaction system of $[\text{Mo}^{\text{VO}}(\text{tpp})]_2\text{O}$ and $\text{Cr}^{\text{II}}(\text{tpp})$ in $\text{C}_6\text{D}_5\text{CD}_3$ because $\text{Cr}^{\text{II}}(\text{tpp})$ exhibits paramagnetism¹⁵ as well as $[\text{Mo}^{\text{VO}}(\text{tpp})]_2\text{O}$ having d^1 electronic state. However, when an excess of $\text{Cr}^{\text{II}}(\text{tpp})$ was mixed with the solution of $[\text{Mo}^{\text{VO}}(\text{tpp})]_2\text{O}$, the formation of $\text{Mo}^{\text{IV}}\text{O}(\text{tpp})$ was confirmed by the characteristic signals at 9.05 (s, pyrrole, β -H), 8.06 and 7.96 (m, phenyl, o -H), and 7.49 ppm (m, phenyl, m -, p -H) vs TMS. The reactions gave no signals of diamagnetic $\text{Cr}^{\text{IV}}\text{O}(\text{tpp})$ because of the formation of paramagnetic $[\text{Cr}^{\text{III}}(\text{tpp})]_2\text{O}$.

UV-vis spectral measurements also confirmed the oxygen-atom transfers from $[\text{Mo}^{\text{VO}}(\text{tpp})]_2\text{O}$ to $\text{Cr}^{\text{II}}(\text{oep})$.



Because of the nearly linear $\text{O}=\text{Mo}-\text{O}-\text{Mo}=\text{O}$ bond of $[\text{Mo}^{\text{VO}}(\text{tpp})]_2\text{O}$ ¹⁶ and of bulkiness of reactant porphyrin ligands, the transfer of bridging oxygen (μ -oxo) atom of $\text{O}=\text{Mo}-\text{O}-\text{Mo}=\text{O}$ to $\text{Cr}(\text{por})$ is unlikely. The mechanism involving terminal oxygen atom transfers was then suggested for the reactions of eqs 4 and 6 as follows.



Oxomolybdenum complexes with non-porphyrin ligands such as dithiocarbamates shows variety of reaction aspects, i.e., incomplete and complete oxygen-atom transfer reactions depending on reactants and encumbrance of ligands.^{2,3} Thus detailed mechanism of oxygen-atom transfer reactions in the present work is of very interests.

References and Notes

- Abbreviations: ttp = 5,10,15,20-tetratolylporphyrinato dianion; tpp = 5,10,15,20-tetraphenylporphyrinato dianion; oep = 2,3,7,8,12,13,17,18-octaethylporphyrinato dianion; M, M' = metal ions.
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- $[\text{Mo}^{\text{VO}}(\text{tpp})]_2\text{O}$ in toluene is photoreduced with visible light to $\text{Mo}^{\text{IV}}\text{O}(\text{tpp})$. T. Imamura and K. Sasaki, unpublished results.
- Due to the importance of high purity and accurate molar-extinction coefficients for this study, the syntheses and the revised UV-vis bands in toluene are described briefly. Elemental analyses of the complexes synthesized were satisfied. $[\text{Mo}^{\text{VO}}(\text{tpp})]_2\text{O}$ was prepared by the dehydration of $\text{Mo}^{\text{VO}}(\text{tpp})\text{OH}$ obtained from $\text{Mo}^{\text{VO}}(\text{tpp})\text{Br}$. UV-vis / nm: 347 ($\epsilon/10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1} = 55.3$), 410 (58.9), 445 (120), 585 (57.8), 615 (6.12), 662 (3.47). $\text{Mo}^{\text{IV}}\text{O}(\text{tpp})$ was prepared by the pyrolysis of $\text{Mo}^{\text{VO}}(\text{tpp})\text{OCH}_3$ in the vessel connected to a vacuum line.⁹ UV-vis / nm: 431 (347), 554 (16.3). $\text{Cr}^{\text{IV}}\text{O}(\text{oep})$ was prepared by the oxidation of $\text{Cr}^{\text{III}}(\text{oep})\text{Cl}$ using iodosobenzene.¹⁰ UV-vis / nm: 416 (112), 535 (6.18), 572 (22.4). $\text{Cr}^{\text{IV}}\text{O}(\text{tpp}) \cdot 0.5\text{C}_6\text{H}_5\text{CH}_3$ was prepared from $\text{Cr}^{\text{III}}(\text{tpp})\text{Cl}$ using $\text{Zn}(\text{Hg})$ followed by air oxidation.¹¹ UV-vis / nm: 376 (14.8), 432 (216), 545 (12.5). $\text{Cr}^{\text{II}}(\text{por})$ was prepared by the pyrolysis of corresponding $\text{Cr}^{\text{III}}(\text{por})\text{N}_3$.¹² UV-vis / nm of $\text{Cr}^{\text{II}}(\text{tpp})$: 423 (315), 542 (4.95). UV-vis / nm of $\text{Cr}^{\text{II}}(\text{oep})$: 331 (sh, 16.4), 349 (19.0), 390 (sh, 32.7), 409 (215), 530 (3.62), 560 (3.19), 729 (2.65).
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