Communications to the Editor

Chem. Pharm. Bull.
32(10)4226—4228(1984)

SPECTROPHOTOMETRIC EVIDENCE FOR THE FORMATION OF A SUPEROXIDE ADDUCT OF CHROMIUM(III) TETRAPHENYLPORPHYRIN COMPLEX

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This is the first report of the reaction of the superoxide ion (O_2^-) with chloro-5,10,15,20-tetraphenylporphyrinatochromium(III), Cr(III)(TPP)Cl, in dimethyl sulfoxide (DMSO) to give the superoxide adduct Cr(III)(TPP)(O_2^-)Cl.

KEYWORDS—superoxide ion; O_2^-; chloro-5,10,15,20-tetraphenylporphyrinatochromium(III); Cr(III)(TPP)Cl; visible spectrum; superoxide adduct; Cr(III)(TPP)(O_2^-)Cl; oxygenated hemoglobin; oxygenated cytochrome P_{450}

The superoxide ion (O_2^-) does not usually function as a substrate for hemoproteins, but the metal-O_2^- center is formally involved in oxygenated hemoglobin and cytochrome P_{450}.[1] If the superoxide adduct could be produced during the reaction of O_2^- with metalloporphyrins, these superoxide adducts would be good models for the oxygenated hemoglobin and cytochrome P_{450}. Recently, it has been reported that Cr(II)(TPP)(py)(O_2)[2] which is prepared from Cr(II)(TPP)(py) and molecular oxygen may exist in the state of Cr(III)-O_2^-.[3] If this is true, the direct formation of the superoxide adduct by the reaction of O_2^- with Cr(III)(TPP)Cl may be possible. Therefore, we have examined in detail the reaction of O_2^- with Cr(III)(TPP)Cl in dimethyl sulfoxide (DMSO) by ultraviolet(UV)/visible spectrophotometry and found the formation of the superoxide adduct, Cr(III)(TPP)(O_2^-)Cl.

UV/visible spectra were measured with a Union Giken SM-401 spectrophotometer at room temperature. The superoxide ion was prepared from KO_2 which was solubilized by dicyclohexyl-18-crown-6 in DMSO[4-7] and its concentration was determined by the reduction method of ferricytochrome c.[5] Cr(III)(TPP)Cl was prepared by the method of Basolo and co-workers[8] and purified by column chromatography on silica gel with chloroform ($CHCl_3$) as eluent. Using a microsyringe, aliquots of O_2^- solutions (10^{-3} - 10^{-2} M) were introduced into 2 ml of Cr(III)(TPP)Cl solution (10^{-6} - 10^{-5} M) in a capped quartz cuvette with a light path of 10 mm. The reactions were started by shaking the cuvette vigorously, and visible spectra were recorded immediately.

When O_2^- solutions were successively added to Cr(III)(TPP)Cl, the visible spectrum changed with isosbestic points (402, 441 and 460 nm)[9] as shown in Fig. 1.

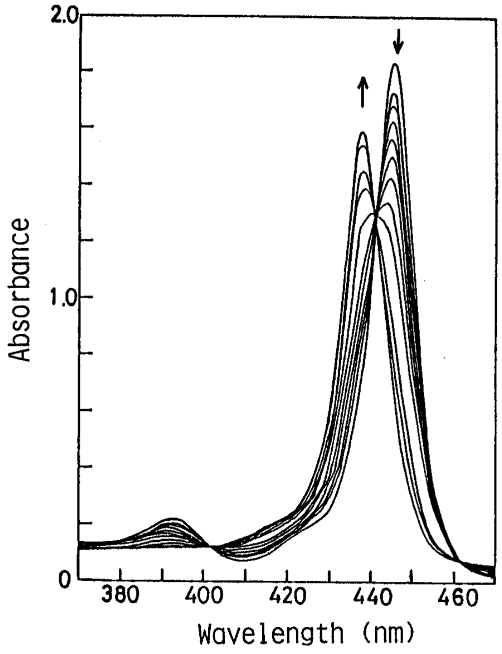

Fig. 1. Absorption Spectral Changes of Cr(III)(TPP)Cl Accompanying with the Titration with O_2^-

2 μl of O_2^- solution was successively added to 2 ml solution of Cr(III)(TPP)Cl in DMSO.

Starting concentration:

Cr(III)(TPP)Cl, 1.0×10^{-5} M;

O_2^-, 3.2×10^{-2} M.

The Soret band underwent a blue shift and the other bands either a red or a blue shift (Table I). Upon addition of excess pyridine to this reaction solution, the newly observed spectrum was replaced by that of the pyridine adduct Cr(III)(TPP)(py)Cl. The visible spectrum of this new chemical species observed during the reaction of O_2^- with Cr(III)(TPP)Cl is different from that of the TPP complexes of Cr(II), Cr(IV) and Cr(V) (Table I). When the DMSO solution of OH^-, which was prepared from KOH solubilized with crown ether,[10)] was successively added to Cr(III)(TPP)Cl, the spectral changes obtained were similar to those observed upon addition of O_2^- (Table I). It is reasonable to consider that OH^- ligates to the axial position of Cr(III)(TPP)Cl. These results strongly support the idea that the chemical species initially formed upon the reaction of O_2^- with Cr(III)(TPP)Cl is the superoxide adduct Cr(III)(TPP)(O_2^-)Cl. This is the first known evidence that Cr(III) porphyrin directly coordinates with superoxide ion. The spectral shifts accompanying with the formation of Cr(III)(TPP)(O_2^-)Cl are particularly interesting. As mentioned above, the Soret band undergoes a blue region shift and the other bands either a red or a blue shift upon addition of O_2^- (Table I). On the other hand, when O_2^- is added to the non-redox metalloporphyrins such as Zn(II)-, Cd(II)- and Mg(II)-TPP, all the absorption band undergoes a red shift.[4)] The spectrophotometric study of the effect of axial ligation to ZnTPP[16)] and CdTPP[10)] has shown that the red shift of the spectrum derives from the density of the negative charge transferred from the ligand to the porphyrin ring _via_ Zn or Cd atom. Gouterman et al. have shown that shifts in the transition energies and relative intensities of the α and β bands in octaethylporphyrinatotin(VI) halides are related to changes in the electron density on the porphyrin ring.[17)]

Table I. Visible Spectra of Different Oxidation States of Chromium Porphyrins

Cr complex	Solvent	λmax/nm	Ref.
Cr(II)TPP	Toluene	422, 542, 575sh[a], 600sh	11
Cr(III)(TPP)Cl	DMSO	396, 448, 522, 568, 608	This work
Cr(III)(TPP)(O_2^-)Cl	DMSO	415sh, 438, 525, 566, 602	This work
Cr(III)(TPP)(OH^-)Cl	DMSO	391, 443, 528, 563, 602	This work
Cr(III)(TPP)(py)Cl	DMSO	396, 449, 527, 567, 606	This work
Cr(IV)O(TPP)	THF	375, 433, 548, 595	12
	Toluene	433, 546, 580	13
Cr(V)O(TPP)Cl	CH_2Cl_2	418, ∿540	14
Cr(V)N(TPP)	Benzene	421, 542	15
	DMSO	424, 550	This work

a) sh; shoulder.

These results mean that visible spectral changes are related to the electron density on the porphyrin ring. Similarly, the blue shift derived from the O_2^- adduct formation of Cr(III)(TPP)Cl may also be related to the electron density in the porphyrin ring. Further studies with this interesting system are in progress, using electron spin resonance (ESR).

REFERENCES AND NOTES

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2) Abbreviations used: TPP, tetraphenylporphyrin; py, pyridine; DMSO, dimethyl sulfoxide; O_2^-, superoxide ion; UV, ultraviolet; THF, tetrahydrofuran; ESR, electron spin resonance.
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(Received August 27, 1984)