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Superoxide Generation in Metalloporphyrin–Phosphine–Hydroxide–Oxygen Systems

HIROMU SAKURAI* and MASAYUKI SHIBUYA

Faculty of Pharmaceutical Sciences, University of Tokushima, Shomachi 1, Tokushima 770, Japan

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There has been much interest in the chemistry and biochemistry of superoxide, O_2^- [1]. Methods for producing superoxide have been reported in several biochemical and chemical reactions [2] such as xanthine oxidase system, hydrogen peroxide–periodate system, pulse radiolysis of aqueous solution and electrochemical reduction of oxygen in organic solvents. However, little is known about the generation of superoxide in metalloporphyrin complexes, although it is very important to study the mechanisms of oxygen activation in oxidases and oxygenases [3]. The example of superoxide generation in the Os(octaethylporphyrin)(1-methylimidazole)$_2$ system in pyridine–water (99:1) solvent was first reported by Billecke *et al.* [4]. We reported superoxide generation in the systems of Co(tetraphenylporphyrin)(CoTPP)– and FeTPP–thiolate complexes in organic solvents in previous papers [5, 6]. This paper reports a new example of superoxide generation in CoTPP–phosphine–hydroxide anion–oxygen system in acetone. This is the first example of superoxide generation in a metalloporphyrin–phosphine complex.

Aerobic addition of tetrabutylammonium hydroxide (TBAH) to a CoTPP–phosphine complex (Fig. 1a) prepared from CoTPP and triphenylphosphine (Ph_3P) in acetone at room temperature resulted in the formation of a free superoxide species which was detected by the usual ESR spectroscopy measured at 77 K (Fig. 1b). The observed anisotropic g-values ($g_\perp = 2.007$ and $g_\parallel = 2.090$ at 77 K) were the same as those observed in frozen solution [7, 8] and in Co– and FeTPP–thiolate systems [5, 6]. Identical signals due to the superoxide were obtained in the systems containing tri-n-butylphosphine in place of Ph_3P and TBAH in place of KOH (dissolved in methanol). However, superoxide was not detected in the triphenylphosphite-containing system.

On the other hand, aerobic addition of Ph_3P to a CoTPP–OH^- complex (Fig. 1c) prepared from CoTPP and TBAH in acetone at room temperature showed ESR signals due to a superoxide ($g_\perp = 2.007$ and $g_\parallel = 2.090$), which were identical to those obtained by the above procedure. Under nitrogen atmosphere, the ESR signals due to superoxide were not observed in either procedures. Thus superoxide is produced by two procedures in the CoTPP–Ph_3P–OH^-–O_2 system, showing these four components are essential for generation of superoxide.

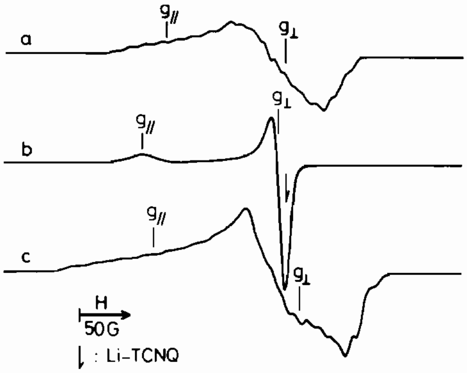

Fig. 1. ESR spectra of superoxide and oxygenated CoTPP–ligand complexes at 77 K. CoTPP(O_2)(Ph_3P) (complex (a)) was prepared from CoTPP (1 mM in $CHCl_3$, 0.1 ml) and Ph_3P (0.5 M in acetone, 0.35 ml). CoTPP(O_2)(OH^-) (complex (c)) was prepared from CoTPP (1 mM, 0.1 ml) and TBAH (1 M in methanol, 0.05 ml). Superoxide (b) was generated with complex (a) by adding TBAH (1 M, 0.05 ml) or with complex (c) by adding Ph_3P (0.5 M, 0.35 ml), under air at room temperature. ESR spectra were measured at 77 K immediately after mixing the components.

Bray *et al.* reported that the $g_\parallel$-value of superoxide shifts markedly towards $g_\perp$ in the presence of some cations, indicating solvent-shared ion pair formation [9]. Judging from the $g_\parallel$-value in the spectrum of superoxide in the present system, it is considered that there is little interaction between superoxide and CoTPP or solvent.

The concentration of superoxide estimated with TANOL (4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl) radical just after mixing and freezing of the reaction mixture was approximately 0.2 mM, showing that superoxide was formed stoichiometrically based on CoTPP concentration. Comparison of the ESR parameters (Table I) of the oxygenated Co(II)TPP–ligand complexes indicated that both Ph_3P and hydroxide coordinate to the axial sixth position *trans* to molecular oxygen binding site to CoTPP and that phosphine is relatively strong ligand to cobalt ion comparable to thiolate ligand [10].

On the basis of the present results, the mechanism for superoxide generation is tentatively proposed, as shown in Scheme 1. The (OH^-)(CoTPP)(Ph_3P) complex as an assumed final product is in ter-valent state and silent in the ESR spectrum. Therefore, the signals due to superoxide are observed in the spectrum. Detection of some intermediate complexes and precise estimation of superoxide generated in

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*Author to whom correspondence should be addressed.

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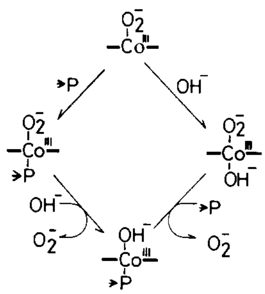
TABLE I. ESR Parameters of Oxygenated Co(II)TPP–Ligand Complexes

Axial ligand	$g_\perp$	$g_\parallel$	$A_\perp$ ($cm^{-1} \times 10^{-4}$) (Gauss)	$A_\parallel$ ($cm^{-1} \times 10^{-4}$) (Gauss)
Triphenylphosphine	2.004	2.075	9.18	14.48
			(9.28)	(14.95)
Hydroxide	1.998	2.085	10.33	20.48
			(11.07)	(21.48)
Thioglycolate ethyl ester[a]				
(-SH Form)	1.990	2.083	10.9	23.1
			(11.7)	(23.8)
($-S^-$ Form)	2.003	2.089	9.7	14.0
			(10.4)	(14.4)

[a] See ref. 10.



Scheme 1. Possible reaction mechanism for superoxide generation in CoTPP–Ph_3P–OH^-–O_2 systems. The $\geqslant$P indicates triphenylphosphine.

the systems are essential for evaluating the superoxide generation. Work is continuing in this line. Furthermore, the production of the free superoxide has also been found by our method using Fe– or Rh–porphyrin complex in place of CoTPP. The mechanisms for these systems are under investigation.

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