

observed for the lead cryptates. This result is most likely a consequence of the lower dielectric constant of the methanol-water mixture compared with water.

ACKNOWLEDGEMENTS

This work was supported in part by the Petroleum Research Fund, administered by the American Chemical Society and the University of Oklahoma Research Council.

REFERENCES

- [1] J.M. LEHN, *Struct. Bonding (Berlin)*, **16**, 1 (1973).
- [2] J.M. LEHN, F. MONTAVON, *Helv. Chim. Acta*, **61**, 67 (1978).
- [3] B. DIETRICH, J.M. LEHN, J.P. SAUVAGE, *J. Chem. Soc., Chem. Commun.*, 15 (1973).
- [4] M. CINQUINI, F. MONTANARI, P. TUNDO, *Gazz. Chim. Ital.*, **107**, 11 (1977).
- [5] M. KIRCH, J.M. LEHN, *Angew. Chem., Int. Ed. Engl.*, **14**, 555 (1975).
- [6] R. GUNTHER, O. HAUSWIRTH, R. ZISKOVEN, *J. Physiol.*, **284**, 145P (1978).
- [7] W.H. MULLER, W.A. MULLER, *Naturwissenschaften*, **61**, 455 (1974).
- [8] PH. BAUDOT, M. JACQUE, M. ROBIN, *Toxicol. Appl. Pharmacol.*, **41**, 113 (1977).
- [9] J.A. DRUMHILLER, J.L. LAING, R.W. TAYLOR, *Anal. Chim. Acta*, **162**, 315-321 (1984).
- [10] C.W. DAVIES, «Ion Association», Butterworths, London, 1962, pp. 39-41.
- [11] B.G. COX, J. GARCIA-ROSAS, H. SCHNEIDER, *J. Am. Chem. Soc.*, **103**, 1054 (1981).
- [12] B.G. COX, P. FIRMAN, I. SCHNEIDER, H. SCHNEIDER, *Inorg. Chim. Acta*, **49**, 153 (1981).
- [13] M.K. CHANTOONI JR., I.M. KOLTHOFF, *Proc. Natl. Acad. Sci. USA*, **78**, 7245 (1981).
- [14] J.M. BEMTGEN, M.E. SPRINGER, V.M. LOYOLA, R.G. WILKINS, R.W. TAYLOR, *Inorg. Chem.*, **23**, 3348 (1984).
- [15] J.A. DRUMHILLER, D.L. LUTON, R.W. TAYLOR, *J. Am. Chem. Soc.*, submitted for publication.
- [16] R. GRESSER, D.W. BOYD, A.M. ALBRECHT-GARY, J.P. SCHWING, *J. Am. Chem. Soc.*, **102**, 651-653 (1980).



PS5.45 — MO

ANDREA MALDOTTI
CARLO BARTOCCI
ALBERTINO FERRI
VITTORIO CARASSITI

Istituto Chimico and Istituto di Chimica Biologica dell'Università di Ferrara
Centro di Studio sulla Fotochimica e Reattività degli Stati Eccitati
dei Composti di Coordinazione del C.N.R.
Via L. Borsari, 46 I 44100 Ferrara
Italy

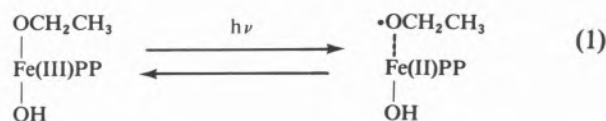
PHOTOCHEMISTRY OF IRON(III) PROTOPORPHYRIN IX IN OXYGENATED ALKALINE AQUEOUS ETHANOL. EVIDENCE FOR SUPEROXIDE RADICAL FORMATION AND ITS INVOLVEMENT IN THE PORPHYRIN DEGRADATION

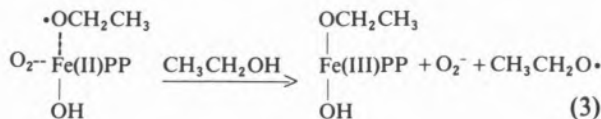
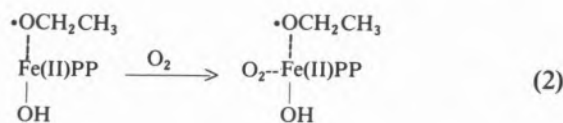
The interest for the formation of superoxide in biological aerobic processes is on steady increase in connection with the auto-oxidation of dioxygen carrier hemoproteins as well as with its toxic effect on living systems.

In recent years, a number of very interesting studies on both the mechanism of formation of superoxide and its reactivity with respect to biological substrates have been reported [1].

We have recently published an ESR-spin trapping investigation on the photochemical behaviour of Fe(III) Protoporphyrin IX chloride (Fe(III)PPCl) in oxygenated water-ethanol mixed solvents [2]. The results obtained in that study allowed us to conclude that Fe(II) porphyrin and an ethoxy radical were formed in the primary photochemical process and that the oxygen interacted somehow with Fe(II) thus hindering a rapid cage back electron transfer. The mechanism proposed is reported in Scheme 1.

Scheme 1





The most interesting aspects in the above scheme are: i) the oxygen should oxidize Fe(II) intermediate when this is still bound to some extent to the ethoxy radical; and ii) superoxide ion should be formed as a product of oxygen reduction.

In the present paper we re-investigate the photochemical behaviour of Fe(III)PPCl in aqueous ethanol for the twofold purpose of having experimental evidence of the superoxide formation and of studying the effect of O_2^- on the porphyrin complex.

Fe(III)PPCl in 40% ethanol/water solvent at pH 12 was irradiated in oxygen atmosphere in an ESR cavity with light of $\lambda > 305$ nm, at room temperature. After 10 minutes of irradiation the solution was quickly cooled to 95 K. In these conditions, an ESR spectrum ($g_{\parallel} = 2.055$, $g_{\perp} = 2.004$), typical of the superoxide radical [3] was obtained. The signal rapidly disappeared when the temperature was raised again to the initial value. These results at the same time confirm the above proposed mechanism and represent the first experimental evidence of superoxide formation upon irradiation of an iron porphyrin. The results obtained in flash-photolysis experiments are also in agreement with the above reported mechanism: in deaerated solution no appreciable photoreduction was observed in a time scale of milliseconds; in oxygenated solution, evidence of formation of Fe(II) porphyrin, which was completely re-oxidized in less than 50 μ sec, was obtained. This indicates that the re-oxidation process occurs via the reaction of oxygen with the coordinatively unsaturated Fe(II) porphyrin intermediate rather than through a bimolecular reaction between dioxygen and a Fe(II) porphyrin complex in some way stabilised prior to oxidation. Prolonged irradiations of Fe(III)PPCl in the above conditions gave rise to an absorbance decrease

in the whole UV-Vis scanned spectral range (300–800 nm). Moreover, the Soret band underwent an evident broadening. This spectral behavior can be taken as an indication of an irreversible modification of the Fe(III) porphyrin complex, consisting in a porphyrin ring opening. Photochemical experiments carried out in alkaline aqueous ethanol containing an excess of imidazole also support the degradation hypothesis: in fact, an absorption band at 670 nm, which could be ascribed to a degradation product of an imidazolate Fe(III) porphyrin complex [4], was observed to be formed under irradiation. It is likely that hydrogen peroxide, formed from the dismutation of superoxide, is responsible for the ring opening process. A similar degradation of an iron porphyrin was demonstrated previously by other authors [5].

REFERENCES

- [1] D. DOLPHIN, B.R. JAMES, H.C. WELBORN, in K.M. KADISH (ed.) «Electrochemical and Spectrochemical Studies on Biological Redox Components», ACS Advances in Chem. Ser. n.° 201, ACS, Washington D.C., 1982, p. 563 and references therein.
- [2] A. MALDOTTI, C. BARTOCCI, R. AMADELLI, V. CARASSITI, *Inorg. Chim. Acta*, **74**, 275 (1983).
- [3] G.W. EASTLAND, M.C.R. SYMONS, *J. Phys. Chem.*, **81**, 1502 (1977).
- [4] S. SANO, Y. SUGIURA, *J. Chem. Soc., Chem. Commun.*, 750 (1982).
- [5] R.F. PASTERNAK, B. HALLIWELL, *J. Am. Chem. Soc.*, **101**, 1026 (1979).



PS5.46 — TH

JOHN H. DAWSON
ELISABETH T. KINTNER
MAUREEN K. GENO
Department of Chemistry
University of South Carolina
Columbia, South Carolina 29208
U.S.A.

BINUCLEAR RUTHENIUM ALKYL DIOXIME COMPLEXES: MODELS FOR ELECTRON TRANSFER THROUGH SATURATED BARRIERS

A question of particular interest to the study of the mechanism of electron transfer in metalloproteins is the nature of the intervening groups and the distance separating redox-active transition metals. We are interested in the distance dependence of intramolecular electron transfer through saturated barriers. The electron density surrounding the metal centers of existing models [1] for electron transfer through saturated barriers is very different from that found in the Fe-Porphyrin or Fe-S prosthetic groups of electron transfer proteins [2]. We have used the (bpy)₂Ru(II) (bpy = 2,2'-bipyridine) moiety instead of (NH₃)₅Ru(II) [3] in order to better mimic the electron density of the protein prosthetic group. Thus we have synthesized a series of binuclear ruthenium alkyl dioxime complexes in which the bridging ligands are the monocyclic 1,4-cyclohexanedione dioxime (cyclodiox), the bicyclic 1,4- and 1,5-substituted *trans* decalindione dioximes (decadiox), and the tetracyclic 5 α -3,17-androstanedione dioxime (androdiox). This provides a series of binuclear metal complexes with the metals separated by a barrier of variable distance. The results of cyclic voltammetric studies of these complexes are shown in Table I. The potential differences for the mono- and bicyclic 1,4-bridged complexes are 471 and 325 mV, respectively with the latter being an irreversible process. The

tetracyclic and 1,5-bicyclic dimers display reversible redox behavior. In the steroid case the two waves nearly coalesce. Overall these data suggest that as the distance between the ruthenium centers increases, the difference in potential decreases.

Table I
Cyclic voltammetry of Ru dimers

Bridge	E _{1/2} (V vs SCE)	
1,4-cyclohexanedione dioxime	.685,	.214
1,4-decalindione dioxime	.950,	.625
1,5-decalindione dioxime	.960,	.770
5 α -3,17-androstanedione dioxime	.900,	.827

Addition of one equivalent of Ce(IV) to the doubly reduced species generates a mixed-valence Ru^{II}-Ru^{III} dimer which is expected to display near-IR intervalence charge transfer (IT) bands. Results for the mono- and tetracyclic Ru dimers are shown (Table II). The extent of delocalization of the exchanging electron (α^2) can be estimated from the properties of the IT band [5] according to the equation (1) [6]

$$\alpha^2 = \frac{4.2 \times 10^{-4} \epsilon_{\max} \tilde{\nu}_{1/2}}{d^2 \tilde{\nu}_{\max}} \quad (1)$$

where d is the Ru-Ru internuclear separation (in Å, based on crystal structure data of the oximes), ϵ_{\max} is the molar absorptivity at the wavelength maximum and $\tilde{\nu}_{1/2}$ is the bandwidth at half-height. The values of α^2 for the mono- and tetracyclic ruthenium dimers (Table II) differ by three orders of magnitude, suggesting that the mixed-valence state is more delocalized in the monocyclic diruthenium complex than in the ruthenium steroid dimer.

Table II

Ru dimer	ΔE (Volts)	$\tilde{\nu}_{\max}$ (nm)	ϵ (M cm) ⁻¹	α^2 (Å ² M cm) ⁻¹
Ru ₂ (μ 1,4-cyclodiox)	.471	910	42	1.3 \times 10 ⁻³
Ru ₂ (μ 3,17-androdiox)	.073	718	3.5	2.6 \times 10 ⁻⁶

These Ru₂(bpy)₂-dioxime dimers represent a new series of ligand complexes with which to study the distance dependence of intramolecular electron transfer through saturated barriers. As the dis-