Journal of

The Chemical Society,

Chemical Communications

NUMBER 1/1973 3 JANUARY

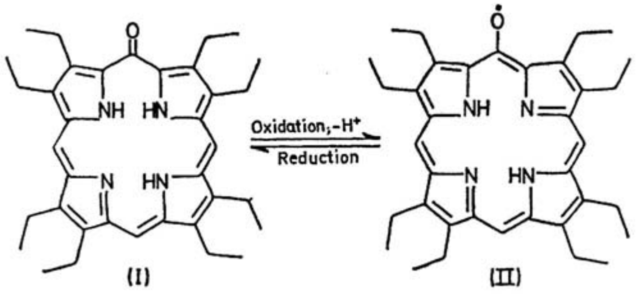
A Stable Octaethyloxophlorin Radical

By J.-H. FUHRHOP,* S. BESECKE, and J. SUBRAMANIAN

(*Gesellschaft für Molekularbiologische Forschung,* 3301 *Stöckheim über Braunschweig, BRD*)

Summary Octaethyloxophlorin (I) yields the stable radical (II) on aerial oxidation; traces of such autoxidation products are considered to account for the paramagnetism reported for oxophlorins.

THE paramagnetic character of oxophlorins has been unresolved for some years;[1,2] *e.g.* octaethyloxophlorin (I) has been shown to contain *ca* 1% of a paramagnetic species at 20°.[2] We now report the preparation of a stable oxidized form of this compound, which exists completely in the free-radical form, and which renders unnecessary the assumption of any special inherent property of the oxophlorin system.



The blue solution of (I) in CH_2Cl_2 was oxidized by air in the course of chromatography on alumina to a pale green solution containing (II) with the spectrum shown in the Figure. Addition of small amounts of triethylamine led to full recovery of the starting oxophlorin (Figure), whereas addition of zinc acetate produced an absorption maximum at 810 nm. The latter compound was also formed on direct oxidation of the zinc octaethyloxophlorin with oxygen or bromoacetamide.

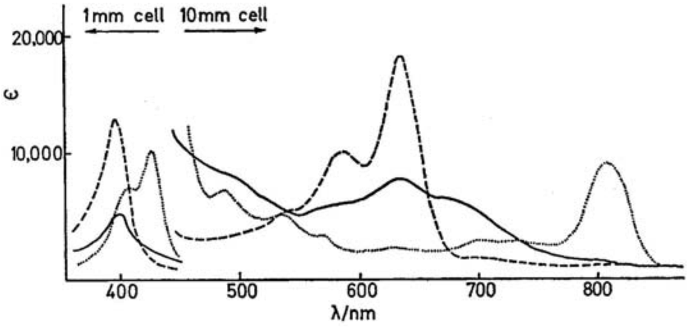


FIGURE. *Electronic spectrum of octaethyloxophlorin in* Bu^tOH: ——— *oxidised form* (II) (*free radical*); – – – – – *reduced form* (I); · · · · · Zn *complex of the radical.*

The crystallized oxidation product decomposed at *ca.* 270° and gave satisfactory elemental analyses. The magnetic susceptibility (1·6 B.M.) and the area of the e.s.r. signal of solutions of (II) in $CHCl_3$ clearly pointed to a full single electron per molecule ($\geqslant$ 70%). In presence of triethylamine[3] no e.s.r. signal was detected. The polarographic oxidation potential of the ketone (I) was found to be −50·0 mV *vs.* SCE, which explains the easy formation of radical (II) in butyronitrile solution. This potential is some 600 mV lower than that for the corresponding porphyrin and indicates an important destabilization of the macrocyclic system through the introduction of a keto-bridge instead of the methine bridge. The *g*-value of (II)

(2·0034 in $CHCl_3$) and the hyperfine structure and coupling constants were identical with those given by Bonnett *et al.*[2] These findings clearly explain the partial paramagnetism of (I), which always contains (II) as an impurity, which is difficult to detect. The chemistry of the stable radical (II) and its metal complexes is currently under investigation. Radical (II) is easily oxidised further to the stable $\alpha\gamma$-dioxoporphodimethene, which has been prepared earlier by a different pathway,[4] and which could be the unidentified red product of the air oxidation of (I) described by Bonnett.[2] Another point which has to be clarified is the temperature dependence of the equilibrium (I) $\rightleftharpoons$ (II) or the possibility that (II) can dimerize, because Bonnett[2] reported such a dependence of the e.s.r. spectrum of his paramagnetic species. First experiments in this direction yielded the expected result, that more radical (II) is formed on heating a solution of a mixture of (I) and (II), whereas at −40 °C the intensity of the e.s.r. signal is less than 10% of that at room temperature.

(*Received*, 6*th October* 1972; *Com.* 1707.)

[1] H. H. Inhoffen, J.-H. Fuhrhop, and F. v. d. Haar, *Annalen*, 1966, **700**, 92; P. S. Clezy, A. J. Liepa, and G. A. Smythe, *Austral. J. Chem.*, 1966, **19**, 1481; A. H. Jackson, G. W. Kenner, and K. M. Smith, *J. Chem. Soc.* (*C*), 1968, 302.

[2] R. Bonnett, M. J. Dimsdale, and K. D. Sales, *Chem. Comm.*, 1970, 962.

[3] J.-H. Fuhrhop and D. Mauzerall, *J. Amer. Chem. Soc.*, 1969, **91**, 4174.

[4] J.-H. Fuhrhop, *Chem. Comm.*, 1970, 781.