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Liberation of the Superoxide Anion from the Dioxygen–Co(II)–Tetrasulfophthalocyanine Adduct in Dimethyl Sulfoxide

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In spite of the fact that the transfer of the first electron to the dioxygen molecule is thermodynamically unfavourable ($\Delta G^\circ_{aq} = 30.54$ kJ/mol, $\Delta G^\circ_{DMSO} = 48.2$ kJ/mol), the superoxide ion O_2^- occurs as an intermediate in some dioxygen reactions, including aerobic processes of biological importance. Studies on the superoxide ion often take advantage of its relative stability in aprotic solvents [1]. Hyland and Auclair [2] have reported generation of the ion in alkaline air-saturated dimethyl sulfoxide (DMSO). The supposed reaction paths (electron transfer from sulfinyl carbanion and/or hydroxyl ion to oxygen) do not take into account the influence of metal impurities, although it can be expected that the production of superoxide ion involves the formation of dioxygen adducts with transition metal complexes.

The present work originated from the finding that Co(II)–tetrasulfophthalocyanine (CoTSP) forms reversible dioxygen adducts in both non-aqueous [3] and aqueous [4] solutions. The aim was to elucidate if and how the dioxygen adduct formation is connected with the generation of free superoxide ion and how it can be affected.

Experimental

Co(II)–tetrasulfophthalocyanine was prepared and purified by a standard procedure [5]. Dimethyl sulfoxide (Merck, zur Analyse) was used without further purification; the declared water content was 0.03%. The reaction components were dissolved in DMSO, except for NaOH which was added in the form of an aqueous solution. 5,5-Dimethyl-1-pyrroline *N*-oxide (DMPO) was prepared and purified according to ref. 6.

ESR spectra were measured on an ERS-220 (GDR) or a Varian E3 spectrometer in the X-band at 77 K. In the presence of a spin trap, the measurements were carried out at room temperature.

Results and Discussion

The ESR spectrum of Co(II)TSP in DMSO under nitrogen corresponds to that reported in ref. 7. At variance with ref. 7, however, bubbling of oxygen through the solution caused a change in the ESR spectrum (Fig. 1a, b), due apparently to the formation of a superoxide-type oxygen adduct usually represented by the formula Co(III)TSP·O_2^- [3]. In our experiments the formation of this adduct was found to be reversible, and the oxygenation–deoxygenation cycle could be repeated several times.

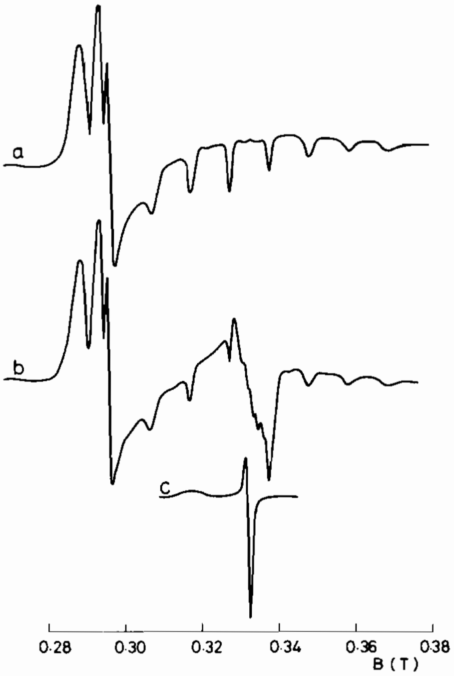

Fig. 1. ESR spectra of CoTSP, dioxygen adduct CoTSP·O_2 and free superoxide ion in DMSO: (a) CoTSP in DMSO, N_2 atmosphere; (b) after bubbling with O_2: CoTSP·O_2; (c) after addition of KCN: O_2^-. [CoTSP] = 1×10^{-3} mol dm^{-3}, [KCN] = 9×10^{-3} mol dm^{-3}, temperature = 77 K.

Upon addition of KCN in about ten-fold excess to the oxygenated solution, the spectra of both CoTSP and CoTSP·O_2 disappear and a new spectrum typical [2] of free O_2^- with $g_\perp = 2.0070$ appears (Fig. 1c). The addition of KCN to oxygenated DMSO in the absence of CoTSP does not produce any O_2^-. The release of superoxide ion after addition of KCN to CoTSP·O_2 has been confirmed by measurements using the spin trapping technique. In the presence of DMPO, the ESR spectrum of the spin adduct DMPO–O_2^- is observed (Fig. 2), with coupling constants ($a_N = 1.27$ mT, $a_H^\beta = 1.03$ mT, $a_H^\gamma = 0.14$ mT), comparable with those compiled in ref. 8. That

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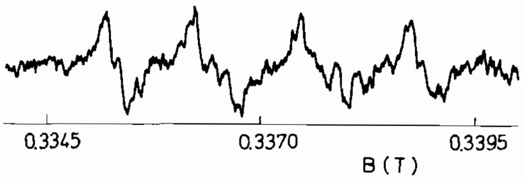


Fig. 2. ESR spectrum of the spin-adduct DMPO–O_2^- in DMSO; [CoTSP] = 1×10^{-3} mol dm^{-3}. [KCN] = 9×10^{-3}, temperature = 25 °C.

DMPO reacts only with free O_2^- and not with the adduct CoTSP·O_2 itself, has been proved by blanks containing only CoTSP·O_2 (without KCN).

In the absence of oxygen, the addition of KCN to CoTSP yields an ESR spectrum with a hyperfine structure ascribed to a CoTSP complex with the cyanide bound on the axial coordination places [7]. When oxygen is admitted into the system, the further behaviour is dependent on KCN concentration. At about ten-fold excess of KCN over CoTSP ([CoTSP] = 9.1×10^{-4} mol dm^{-3}, [KCN] = 9.0×10^{-3} mol dm^{-3}), an axially symmetrical spectrum of O_2^- appears after 30 s of bubbling oxygen and rapid freezing to 77 K. This is the same result as observed on addition of KCN to the oxygenated solution of CoTSP. At comparable concentrations of both components ([CoTSP] = 9.1×10^{-4} mol dm^{-3}, [KCN] = 1×10^{-3} mol dm^{-3}), oxygenation of the solution produces superimposed spectra of Co(II)TSP and CoTSP·O_2 (see Fig. 1b). A ten-fold smaller concentration of KCN ([CoTSP] = 9.1×10^{-4} mol dm^{-3}, [KCN] = 1×10^{-4} mol dm^{-3}) has no effect on the ESR spectra.

Hydroxyl ions added to an oxygenated solution of CoTSP in DMSO containing the adduct CoTSP·O_2 have the same effect as CN^- ions, namely the disappearance of the CoTSP and CoTSP·O_2 spectra and the appearance of the O_2^- signal at 77 K. Its intensity is substantially higher in the presence of CoTSP than in pure alkaline DMSO. The dependence of the relative intensity of the O_2^- signal on the CoTSP concentration is represented in Fig. 3. At the highest concentration of CoTSP ($<4 \times 10^{-4}$ mol dm^{-3}), the spectra of the superoxide ion and the adduct CoTSP·O_2 overlap. The sigmoid shape of the profile indicates the existence of an equilibrium between several components. The concentration of O_2^- in the system estimated on the basis of a Mn standard ranged from 5×10^{-6} to 2×10^{-5} mol dm^{-3} for [CoTSP] = 1×10^{-5} to 1×10^{-4} mol dm^{-3}.

Free O_2^- is also formed by oxygenation of an oxygen-free solution of CoTSP in alkaline DMSO. At higher CoTSP concentrations, the O_2^- is superimposed on a weaker spectrum of CoTSP·O_2. The initial oxygen-free solution is ESR silent. Thus, in the system containing CoTSP, O_2 and CN^- or OH^- in DMSO, the superoxide ion is produced independently of the sequence in which the components are added. Imidazole used as ligand instead of CN^- or OH^- enhances the concentation of the oxygen adduct, but no O_2^- has been detected.

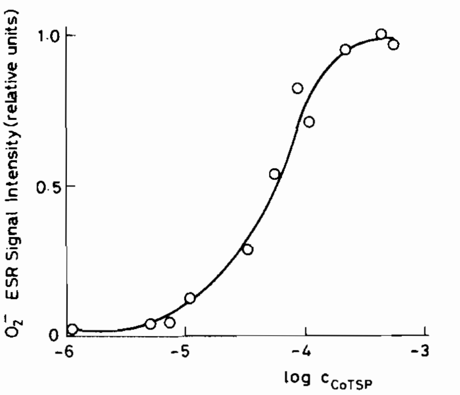


Fig. 3. A plot of the relative intensity of O_2^- ESR signal vs. CoTSP concentration; [NaOH] = 1×10^{-2} mol dm^{-3}.

The above results indicate clearly that the free superoxide ion originates via a superoxide-type oxygen adduct CoTSP·O_2. The reaction described in ref. 2 can proceed in parallel, but has a substantially lower yield. The ligand occupying the axial coordination place affects the electron density distribution along the axis [9], and thus the strength of the Co–O_2 bond.

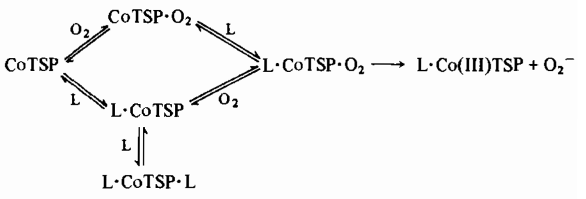
Depending on its donor properties (and probably the properties of the solvent) an axial ligand can cause:

(i) a complete one-electron transfer from metal to dioxgyen, i.e. the formation of O_2^- and Co(III)-TSP, as in the case of CN^- and OH^-;

(ii) a change in the electron density leading to an enhancement of the adduct CoTSP·O_2 concentration, as in the case of imidazole;

(iii) a complete two-electron transfer from axial ligand to dioxygen, i.e. the catalytic oxidation of the ligand, as in the case of e.g. ascorbic acid [10].

The formation of the superoxide ion in our system can be represented by reaction Scheme 1:



Scheme 1. L = CN^-, OH^-

The upper reaction path (via CoTSP·O_2) corresponds to the addition of a ligand to an oxygenated solution, while the lower part represents oxygenation of an oxygen-free solution containing the ligand. The only hypothetical species in this scheme is the short-lived intermediate (the ternary complex L·CoTSP·O_2) in which the electron transfer occurs. Since the electron is transferred from the metal and not from the ligand, the reaction is stoichiometric (non-catalytic). The disappearance of the Co(II) spectrum after addition of excess ligand is in agreement with the formation of ESR-silent Co(III).

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