EPR STUDY OF REDUCTION OF VANADYL TETRASULPHOPHTHALOCYANINE BY ASCORBIC ACID

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Based on the EPR spectra, vanadyl tetrasulphophthalocyanine (VOTSP) was found to be reduced by ascorbic acid in alkaline medium to the vanadium(III) complex. The hyperfine structure of the spectra indicates that after re-oxidation, the equilibrium between the dimeric and the monomeric forms of VOTSP is shifted in favour of the latter as compared with the initial state, obviously owing to the formation of adducts of VOTSP with the oxidation products of ascorbic acid. The formation of the adducts prevents dimerization.

During a study of the kinetics and mechanism of the autooxidation of ascorbic acid catalyzed by vanadyl tetrasulphophthalocyanine (VOTSP), a mixed-ligand (ternary) complex involving VOTSP, ascorbic acid, and molecular oxygen in the ratio 1 : 1 : 1 has been identified spectrophotometrically in the reaction system[1]. The stopped-flow method has been used to prove that this ternary complex is a reactive intermediate of the reaction, kinetically capable of taking part in the catalytic cycle. In this connection the question arises as to in which oxidation state vanadium occurs in the ternary complex and in which manner the substrate and/or molecular oxygen are bound. In fact, VOTSP possesses an octahedral structure in which one axial coordination site is occupied by the oxygen of the vanadyl group and only one axial coordination site remains free for the bonding of either substrate, so that only a binary adduct should be formed rather than the ternary complex.

In the present work, the EPR spectroscopy technique has been employed with the aim to determine the oxidation state of vanadium in the reaction mixture with ascorbic acid and to find in which way the substrates can be bound in the ternary complex.

The EPR spectrum of vanadium in the oxidation state IV (d^1 system) consists of eight lines of the hyperfine structure, in accordance with the nuclear spin $I_N = 7/2$. In the case of VOTSP, a spectrum exhibiting the hyperfine structure can be obtained only if the substance is dissolved in a nonaqueous medium, preventing its dimerization, or in a mixture of a solvent such as dimethylformamide or dimethyl sulphoxide with water. In aqueous solutions, practically all metal tetrasulphophthalocyanines form

dimers or higher polymers arranged axially, with interplanar distances 0·43 nm in CuTSP and 0·45 nm in VOTSP (ref.[2]). VOTSP in diluted aqueous solutions (10^{-5}M) exists practically in the dimeric form, the fraction of higher polymers increasing with concentration. The EPR spectrum of VOTSP in water displays a broad singlet signal[2]. Vanadium in the oxidation state III, like other d^2 ions, yields an EPR signal only at 4·2 K.

EXPERIMENTAL

VOTSP tetrasodium salt was prepared and purified according to[4]. All other chemicals were reagent grade purity. Stock solutions of ascorbic acid (Pharmakon, Czechoslovakia; Index Pharm. 3) were freshly prepared every two days and stored in darkness at 5°C. Conductivity of redistilled water used was below 2 μS cm^{-1} at 25°C.

Preliminary measurements of the EPR spectra of VOTSP in aqueous solutions at room temperature and at 77 K were performed at the Central Institute of Molecular Biology, Academy of Sciences of the GDR, on a self-constructed apparatus[3]. The other measurements were carried out on a JEOL JES-3B EPR spectrometer (Japan) in the X-band ($\nu \approx 9{\cdot}2$ GHz), modulation frequency 100 kHz, microwave power 1·5 mW, temperature 103 K. A Mn^{2+} standard (JEOL) and crystalline diphenylpicrylhydrazyl ($g = 2{\cdot}0036$) were used for the calibration. The samples to be measured were placed in quartz cells, outer diameter 5 mm. Prior to mixing, the aqueous solutions of the components were freed from oxygen by bubbling with nitrogen. Mixing of the components and cooling down of the samples was carried out in nitrogen atmosphere. In some cases, oxygen was led into the samples already measured and de-iced and the samples were cooled down again for measurement. The samples measured contained $5 \cdot 10^{-3}$ — $1 \cdot 10^{-2}$M-VOTSP, 0·1M ascorbic acid, and 0·4M-NaOH. Owing to the concentration of hydroxyl ions, ascorbic acid (pK_1 4·04, pK_2 11·34) was present predominantly in the form of the dianion.

RESULTS AND DISCUSSION

Aqueous solutions of vanadyl sulphate yield at room temperature an EPR spectrum with eight lines, in accordance with the spectra of other V(IV) compounds[2]. The spectrum is not affected appreciably by the presence of ascorbic acid; if, however, the ascorbic acid-containing solution is alkalized, the EPR signal disappears instantly in the case of the sulphate and with intens of minutes in the case of the oxalate. The vanishing of the signal is obviously due to reduction of V(IV) to V(III) by ascorbic acid in alkaline medium. Addition of ascorbic acid as well as the alkalization is associated with a colour change.

Solutions of VOTSP, containing predominantly the dimeric species $(VOTSP)_2$, give rise to a broad singlet signal at 103 K, the character of which does not change essentially with pH ($g = 1{\cdot}988$). The spectrum of an alkaline solution is steady for several hours. In alkaline solution, the signal decreases substantially on adding ascorbic acid, but it does not disappear completely even if the work is conducted under nitrogen (Fig. 1). The g-factor does not change as the intensity lowers. However, there appears a new narrow signal ($g = 2{\cdot}0101$), not occurring in the initial spectrum of VOTSP or ascorbic acid.

After bubbling the reaction mixture with oxygen, the original singlet signal of $(VOTSP)_2$ is restored. The cycle of the reduction with ascorbic acid and re-oxidation with oxygen, accompanied by the decrease and increase in the signal intensity, can be

TABLE I

The g-Factors of the EPR Signals Obtained at Different Conditions

System	g-Factor	
	singlet signal	hyperfine splitting
VOTSP without ascorbic acid	1·988	2·0201[a]
After re-oxidation of the reaction mixture by oxygen	1·9875	2·0067
VOTSP + dehydroascorbic acid	1·9881	2·0079[b]

[a] In 50% DMF–water solution, splitting constant $a = 5{\cdot}41$ mT; [b] splitting constant $a = 4{\cdot}21$ mT.

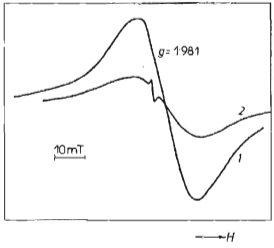

FIG. 1

EPR Spectrum of the Dimeric $(VOTSP)_2$ in Aqueous Solution

0·01M-VOTSP, 0·4M-NaOH; measured at 103 K under nitrogen; *1* $(VOTSP)_2$, *2* $(VOTSP)_2$, 0·1M ascorbic acid.

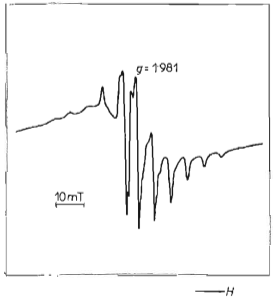

FIG. 2

EPR Spectrum of VOTSP in the Presence of Dehydroascorbic Acid

0·005M-VOTSP, 0·4M-NaOH, approx. 0·1M dehydroascorbic acid (saturated solution); measured at 103 K under nitrogen immediately after adding dehydroascorbic acid.

repeated several times. The signal with $g = 2{\cdot}0101$ does not change essentially during the re-oxidation; thus it cannot represent an unresolved doublet of the ascorbate radical[5], since it would have to disappear during the re-oxidation. The initial singlet signal is also restored during the slow re-oxidation occurring when the solution is allowed to stand on air for about 24 h, and a weakly developed hyperfine structure can be observed.

When dehydroascorbic acid, the oxidation product of ascorbic acid, is added under nitrogen to an alkaline solution of VOTSP, the lines of hyperfine splitting appear in the spectrum in addition to the singlet signal (Fig. 2).

The values of the g-factor of the singlet signal and of the hyperfine splitting lines as well as the splitting constant are given in Table I. The g-factor of the hyperfine splitting lines measured in the system VOTSP–50% DMF–water is also given for comparison; in this case the monomeric VOTSP is present in the solution to a high extent[2]. The g-factors of the lines of hyperfine splitting in the spectra of the reaction mixture both after the re-oxidation and after the addition of dehydroascorbic acid are very close, which indicates that the same process, *viz.* interaction of VOTSP with dehydroascorbic acid, is involved in the two cases. Although these g-factor values differ somewhat from those measured in 50%DMF, it can be deduced from the spectral patterns that in this case, too, the hyperfine splitting corresponds to monomeric VOTSP.

The fact that on addition of ascorbic acid to alkaline solutions of monomeric vanadium compounds (vanadyl sulphate or oxalate) or dimeric vanadium compounds the signal of V(IV) vanishes or at least decreases can be ascribed unambiguously to the reduction to V(III), which at 103 K does not yield an EPR signal. This explanation is borne out also by the restoration of the initial signal on the re-oxidation of the sample and by the possibility of repeating the reduction–oxidation cycle, as it was observed during the study[1] of the catalytic properties of VOTSP. Since V(III) complexes also possess an octahedral structure, in V(III)TSP there are two free axial coordination sites, which can be occupied by the two substrates forming the ternary complex [O_2 . VTSP . ascorbic acid]. The fact that unlike simple vanadyl salts, VOTSP is not reduced to V(III)TSP completely, is due either to a different oxidation–reduction potential of the complex or to the effect of dimerization.

In the case of VOTSP, only the monomer undergoes reduction, the dimer being nonreactive[4]. Consequently, the reduction is preceded by an equilibrium between the monomer and the dimer. During the re-oxidation of V(III)TSP the monomeric VOTSP is formed primarily and dimerizes subsequently. Although the dimerization should be very fast[4] (rate constant $k_D = 8{\cdot}4 \,.\, 10^6 \mathrm{M}^{-1}\,\mathrm{s}^{-1}$), the existence of hyperfine structure indicates that after the re-oxidation the equilibrium is shifted more in favour of the monomeric VOTSP than it was in the initial solution. This change is apparently accounted for by the formation of adducts of VOTSP with the products of ascorbic acid oxidation, which are bound on the free axial coordination site and preclude the

dimerization. The assumption that an adduct of VOTSP with dehydroascorbic acid is formed is consistent with the fact that if dehydroascorbic acid is added to VOTSP, the lines of hyperfine splitting belonging to the monomer appear in the spectrum, and that vanadyl itself forms a complex with dehydroascorbic acid ($\log K_1 = 7{\cdot}21\ \mathrm{mol}^{-1}$) (ref.[6]).

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