Photoreduction of Copper Chromophores in Blue Oxidases*

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The low temperature (77 K) irradiation of oxidized ceruloplasmin and Rhus vernicifera laccase at the 330 nm absorption which arises from type 3 copper leads to the reduction of type 1 copper as demonstrated by bleaching of the 610 nm chromophore and the decrease of the EPR signal associated with this species. Type 2 copper remains unaffected. Concomitant with the type 1 copper reduction, a new EPR signal which is possibly that of a biradical appears. Upon thawing, type 1 copper is reversibly oxidized and the radical signal disappears. Irradiation of oxidized protein at the absorption band of type 1 copper produces no spectral change. An EPR study at room temperature confirms the wavelength specificity and reversibility of the photoreduction of type 1 copper and radical formation. Radical appearance and disappearance at room temperature are extremely slow ($\tau_{1/2} \sim 30$ min). Optical studies at room temperature show that upon anaerobic irradiation of laccase in the 330 nm absorption band, both type 3 and type 1 chromophores are slowly reduced. Upon return to the dark and in the presence of O$_2$, both type 3 and type 1 centers are reoxidized. Oxidizing equivalents either from O$_2$ or K$_3$Fe(CN)$_6$ are required for the reoxidation reaction. These studies demonstrate that there is a direct energy transfer between type 3 and type 1 copper sites in blue copper oxidases.

Laccase and ceruloplasmin are blue copper proteins that exhibit oxidase activity. For both of them, single electron oxidation of substrates occurs at the expense of 4-electron reduction of an O$_2$ molecule to yield water as a product of the reaction. This enzymatic reduction of O$_2$ takes place through interactions among the multiple and functionally inequivalent metal sites of these copper proteins.

The use of visible, infrared, and EPR spectroscopy, magnetic susceptibility, as well as oxidation-reduction titrimetry has permitted the distinction of three types of sites in the blue copper-containing oxidases (1, 2). The first, designated as type 2 Cu$^{2+}$, has the usual physical characteristics of simple cupric salts ($\varepsilon = 100$ to 400 m$^{-1}$ cm$^{-1}$, $A_1 = 13 - 20$ mK) (3). The type 3 site is EPR-silent and is thought to consist of a pair of antiferromagnetically coupled Cu$^{2+}$ cations. This last site has a strong optical absorption around 330 nm ($\varepsilon = 3000$ to 5000 m$^{-1}$ cm$^{-1}$). These three types of sites have unusually high oxidation-reduction potentials that can be largely modulated through exogenous ligation and site-site interactions.

Little is known about the respective spatial relationships of the metal ions within the blue copper-containing oxidases other than that the paramagnetic copper cannot be close to each other. As for the specificity of function of individual sites, it has been suggested, through rather indirect evidence, that substrates are bound somewhere near or at the type 1 site, molecular oxygen at the type 3 site, and water, a product of the enzymatic process, is released from the type 2 site (1, 2). Hydrogen peroxide, a suggested intermediate of O$_2$ reduction, is believed to be bound both at the type 2 (4) and type 3 (5) sites. No specific pathway of electron transfer between sites in a given oxidase has as yet been ascertained.

Visible light irradiation of proteins in the presence of photosensitizers and photolabels has been used to probe the topography of many proteins (6, 7). When the active site is itself a chromophore, as it is in the case of the cytochromes, for example, it can be probed directly in the absence of any exogenous photosensitizers by using the light-induced excited state of the chromophore (8). We here report such experiments on blue copper oxidases that demonstrate reversible photoreduction of some of the copper sites and the generation of a radical species.

MATERIALS AND METHODS

Copper proteins were prepared according to standard methods. Ceruloplasmin was purified from porcine sera according to the procedure of Levine and Peisach (9) and from human sera according to the method of Deutsch et al. (10). Laccase from Rhus vernicifera was prepared according to Reinhammar (11). Laccase and ceruloplasmin oxidase activites were assayed according to the methods of Reinhammar (11) and Young and Curzon (12), respectively. In order to avoid reduction at high pH as was observed for fungal laccase (13), all experiments were performed at pH 6.0 or below in phosphate or acetate buffer.

Irradiation studies were performed under a variety of experimental conditions. Mercury high pressure HBO 300-watt lamps were used. The characteristics of the various optical filters used alone or in combination with one another are given in Fig. 1. For irradiation in the visible range, a symmetrical doublet consisting of two identical lenses of 17-cm focal length was used in order to obtain a good image of approximately 2-cm diameter. A quartz water filter of 6-cm thickness was placed anywhere between the two lenses. Illumination at the image was measured with a Chauvin-Arnoux luxmeter. Irradiation at
77 K was performed on frozen protein solutions in a cylindrical 3-mm diameter EPR quartz tube inserted into a quartz Dewar flask either directly in the EPR cavity or outside it. For EPR studies at room temperature, the protein solution was irradiated directly in the EPR cavity in a capillary flat quartz cell of 0.5-mm thickness.

Room temperature optical spectra were recorded with a Cary 118 spectrophotometer. EPR studies were performed on Varian E3, E9, or E109 E spectrometers operating at X band. Modulation amplitudes were 1 or 2 G for spectra recorded at 77 K, and 4 or 10 G for room temperature spectra. Microwave power was usually 1 or 2 milliwatts at 77 K and 10 milliwatts at room temperature. Power saturation experiments were performed at 77 K between 0.5 and 50 milliwatts, 1,1-Diphenyl-2-picrylhydrazyl (DPPH)\(^2\) in benzene was used as a field marker. The magnetic field was determined by use of a proton resonance fluxmeter (Varian F-8) and a frequency counter (Rochal A 1300). EPR spectra were accumulated with a multichannel analyzer Tracer Northern NS 570.

**RESULTS**

**Photoirradiation of Oxidases at 77 K**—Irradiation of ceruloplasmin or lactase at 77 K using the emission spectrum of a mercury lamp (except for the infrared region) leads to the bleaching of the blue color, a decrease of the intensity of the EPR signal ascribed to type 1 Cup\(^+\) (\(g_L = 2.195, A_L = 8.15 \text{ mK}\) for ceruloplasmin), and at the same time, the appearance of a complex new EPR signal, that of a radical species, centered around \(g = 2\) (Fig. 2). Type 2 copper is not affected by the irradiation as shown by invariance of the EPR signal at low field arising from this species (Fig. 2B) (\(g_L = 2.250\) and \(A_L = 17.0 \text{ mK}\)). The appearance of the new radical signal is coinci-

\(^2\) The abbreviation used is: DPPH, 1,1-diphenyl-2-picrylhydrazyl.

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**Fig. 1.** Transmission spectra (solid lines) of the optical filters used for irradiation experiments: Fi 277 (MTO, Intervex, \(\lambda_m = 277 \text{ nm, } \Delta \lambda = 19 \text{ nm, } \tau_m = 0.18\)), Fi 351 (MTO, Intervex, \(\lambda_m = 351 \text{ nm, } \Delta \lambda = 11 \text{ nm, } \tau_m = 0.22\)), J 324 a (MTO, Specivex, \(\lambda_c = 324 \text{ nm}\)), UG 2 (Wood, \(\lambda_m = 356 \text{ nm, } \Delta \lambda = 48 \text{ nm, } \tau_m = 0.56\)), J 326 a (MTO, Specivex, \(\lambda_c = 326 \text{ nm}\)), OG 2 (Wood, \(\lambda_c = 573 \text{ nm}\)). The dashed line represents the absorption spectrum of \(R. \) vernicifera lactase for comparison.

**Fig. 2.** A, EPR spectra at 77 K of porcine ceruloplasmin (4.9 \times 10^{-4} M) in acetate buffer 0.05 M, pH 5.7) under constant irradiation using the full mercury lamp spectrum. Each spectrum was recorded at approximately 30-min intervals. The liquid \(N_2\) dewar was not moved during the whole experiment. For the three initial spectra, the EPR sample tube was irradiated directly in the EPR cavity. For the next five, irradiation was performed outside the cavity in another liquid \(N_2\) dewar. *Inset,* plot of the peak-to-peak amplitude of the copper \(g\), signal against the amplitude of the radical at extrema corrected for the contribution of the copper signal at these points. Microwave power was 10 milliwatts; modulation amplitude, 1 G; microwave frequency, 9.35 GHz. B, low field portion of the EPR spectra at 77 K of irradiated porcine ceruloplasmin. 1, spectrum before irradiation; 2, spectrum after 5-h irradiation. Conditions were the same as in A.
dent with the loss of resonance intensity ascribed to Cu\(^{2+}\) in the region of \(g_s = 2.050\) (Fig. 2). The decrease of the amplitude of \(g_s\) is proportional to the peak-to-peak amplitude of the new signal which is shown with better resolution in Fig. 3A. The main spectral features consist of four lines symmetrically arranged on either side of \(g = 2.004\), two of which are separated by approximately 30 G while the other two are 80 G apart. The radical signal begins to saturate at microwave power greater than 2 milliwatts at 77 K. We are able to show that the EPR signal of Fig. 3A arises from three different free radical species, only one of which is specific to oxidized, but not reduced, blue copper oxidases (see below).

Upon thawing of the irradiated blue copper oxidases, the EPR signals of the radical species disappears and at the same time, both the blue color and the EPR signal of type 1 copper are nearly completely restored. This reversibility demonstrates that irradiation does not induce irreversible degradative processes at the type 1 copper site.

**Radical Formation of Frozen Protein Solutions**—Photoirradiation of a nonmetalloprotein such as bovine serum albumin produces a simple radical signal of 20 G peak-to-peak linewidth centered at \(g = 2.004\). This radical could arise from the protein backbone or from some aromatic residue (14). Irradiation of ceruloplasmin which is reduced by ascorbate gives rise to a similar radical. Under these conditions, the four-line spectrum we observe in the irradiated oxidized protein (Fig. 3A) is not seen. As will be shown later, this type of simple radical can arise from ultraviolet excitation of the protein moiety of the copper oxidases.

The major features of the four-line signal shown in Fig. 3A do not arise from sulfur radicals similar to those produced by \(\gamma\)-irradiation of proteins containing cystine (15). In the case of irradiated blue copper oxidases, this latter type of radical could possibly account for the shoulders indicated by arrows in Fig. 3A, with a relative intensity that varied from experiment to experiment.

Another radical that we observed in frozen protein solutions is generated by the irradiation of a frozen buffer solution. This radical consists of three features centered at \(g = 2.002\) with two side bands situated at 245 G to higher and lower magnetic field. This radical signal may arise from hydrogen atoms (16, 17) which can be generated by irradiation of frozen aqueous solutions. It does not seem to arise from the irradiated quartz. The small amplitude of this radical cannot account for more than 3\% of the amplitude of the overall signal appearing upon irradiation of blue copper proteins.

**Action Spectrum of Bleaching of Blue Copper Oxidases**—Blue copper oxidases were irradiated at selected absorption bands, both at 77 K and at room temperature, in an attempt to have a more comprehensive understanding of the photochemical phenomena observed. Illumination of oxidized ceruloplasmin at 77 K in the ultraviolet band using an interference filter with maximum emission at 277 nm (transmission less than 1\% above 320 nm, Fig. 1) does not bleach the protein but creates a radical which is similar to that obtained with bovine serum albumin or with ascorbate-reduced ceruloplasmin using the whole mercury lamp spectrum. Illumination at wavelengths greater than 572 nm (Wood OG 2 filter, Fig. 1), that is, in the broad absorption band of type 1 copper, results in no detectable effect either on the blue color or on the EPR spectrum. Finally, illumination in the region of the 330 nm absorption band, using Wood UG 2 and J 324 \(\alpha\) filters in tandem (maximum transmission at 358 nm with transmission less than 0.1\% below 312 nm and above 390 nm) or interference filter Fl 351 (Fig. 1) leads to both the bleaching of type 1 Cu\(^{2+}\) and the creation of a four-line radical signal shown in Fig. 3B. This signal produced by narrow band irradiation is similar to the one produced by wide band irradiation which is shown in Fig. 3A. It lacks, however, the narrow absorption band at \(g = 2\), which is seen upon irradiation of the reduced protein, and also the features thought to arise from sulfur radical. As care was taken not to excite the protein ultraviolet bands, this experiment relates the bleaching of the absorption near 610 nm and the appearance of the four-line radical signal specifically to the oxidized copper protein. It also suggests an interaction between the chromophore absorbing at 330 nm (the type 3 copper pair) and that absorbing at 610 nm (type 1 Cu\(^{2+}\)).

**EPR Studies at Room Temperature**—Experiments at room temperature confirm the wavelength specificity of the photo-reduction. As the number of each type of copper sites in ceruloplasmin is still controversial (18), these experiments were performed only on *R. vernicifera* laccase which is known to have one site each of types 1, 2, and 3 Cu\(^{2+}\). Upon illumination of laccase at room temperature using the whole lamp spectrum, a four-line radical signal appears in the EPR. The same result is obtained when the illumination is performed near 350 nm (Fig. 4). However, there is no effect when the illumination is at wavelengths greater than 572 nm, that is, near the type 1 copper absorption band. Due to the low signal to noise ratio of the EPR spectrum taken at room temperature, we could not distinguish type 1 and type 2 copper signals nor could we determine quantitatively the degree of reduction of the copper signals at \(g_s\). Kinetic experiments of the appearance of the radical upon illumination and its reversible disappearance in the dark (Fig. 5) show that both phenomena are exceedingly

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**FIG. 3.** A, EPR spectrum at 77 K of the radical signal arising from porcine ceruloplasmin (protein concentration = \(4.9 \times 10^{-4}\) M, acetate buffer 0.06 M, pH 5.7) after a total illumination time of 5 h outside the EPR cavity using the whole spectrum of a mercury lamp. Microwave power was 1 milliwatt; modulation amplitude, 1 G; microwave frequency, 9.35 GHz. The curved base-line represents the \(g_s\) contribution of the paramagnetic protein copper. B, EPR spectrum of the radical resulting from irradiation at 351 nm of human ceruloplasmin (protein concentration = \(2.2 \times 10^{-5}\) M, acetate buffer 0.05 M, pH 5.5) at 77 K (filter Intervex Fl 351, see Fig. 1) for 4 h. Microwave power was 1 milliwatt; modulation amplitude, 1 G; microwave frequency, 9.14 GHz.

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**Copper Oxidases**

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slow. The amount of illumination on the sample within the EPR cavity could not be measured directly. It was estimated to be between 900 and 500 lux when using filter UG 2 (356 nm transmission). With a protein concentration of the order of $6 \times 10^{-4}$ M, the half-life of the overall radical appearance was between 20 and 50 min. The high viscosity of lactase solutions at the high concentrations used for EPR studies could partially explain its slow appearance and disappearance. It could not explain, however, the optical data in much more dilute solutions (see below).

**Optical Studies at Room Temperature**—Optical studies demonstrate the spectral specificity observed by EPR and furthermore yield information about the fate of type 3 copper. Irradiation at $\lambda_{max} = 358$ nm of a lactase solution in a Thunberg optical cell in the absence of oxygen decreases the absorption at both 610 and 350 nm (Fig. 6), demonstrating that both types 1 and 3 copper are reduced. While photoreduction of the 610 nm chromophore appears as pseudo-first order ($k = 0.5$ h$^{-1}$), that of the 350 nm chromophore is obviously not first order. Due to the complexity of the observed kinetics, no attempt was made at this stage for a detailed analysis. Under aerobic conditions (Fig. 7), the loss of blue color of lactase caused by irradiation is markedly decreased ($k = 0.27$ h$^{-1}$). These experiments suggest that oxygen either inhibits the loss of color or participates in an oxidation-reduction process with the photoreduced protein.

Under anaerobic conditions, the restoration of blue color cannot be achieved in the dark. Introduction of oxygen restores quickly the 330 nm absorption; however, the restoration of the blue color (610 nm) is extremely slow. In contrast, the addition of a crystal of ferricyanide produces an immediate restoration of color. Despite the slowness of both the photoreduction and the reversible reoxidation with O$_2$ in the dark and the fact that a full experiment lasts for several hours at room temperature, a very good reversibility is always obtained based on optical and EPR criteria. It should be pointed out

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**Fig. 4.** A and B, EPR spectra of *R. vernicifera* lactase solution (protein concentration = $6 \times 10^{-4}$ M, phosphate buffer, pH 6.0) at room temperature. Microwave power was 10 milliwatts; modulation amplitude, 10 G; microwave frequency, 9.49 GHz. A, sample not irradiated; B, sample was irradiated for 30 min at 356 nm using filter UG 2; C, EPR spectrum at room temperature of the radical arising from irradiation of a lactase solution. Sixteen spectra were accumulated under continuous irradiation around 356 nm; fifteen spectra of nonirradiated lactase were subsequently subtracted, representing the nonphotoreduced mononuclear Cu$^{2+}$. Modulation amplitude was 4 G, other conditions as in A.

**Fig. 5.** Kinetics of the appearance (*A*) and disappearance (*B*) after return to the dark of a radical produced by irradiation of lactase, at room temperature. Lactase (protein concentration = $6 \times 10^{-4}$ M) in phosphate buffer 0.01 M, pH 6.0, was irradiated continuously within the EPR cavity in a quartz cell of 0.5-mm thickness. The amplitude of the radical was measured between derivative extrema (see Fig. 4) and corrected for the copper signal amplitude difference at these points. A$_1$, A$_2$, and A$_3$ refer to experiments performed without filter, with filter UG 2 ($\lambda_{max} = 356$ nm), and with filter OG 2 ($\lambda_{max} = 573$ nm), respectively (see Fig. 1). A$_1$ represents the amplitude of the radical in a quasi-steady state after 100 min. B, A$_1$ represents the initial amplitude of the radical at the end of the experiment represented in A.

**Fig. 6.** Effect of irradiation at 358 nm (filters UG 2 and J 324 used together) on a *R. vernicifera* lactase solution deoxygenated in a quartz Thunberg cell (4-mm lightpath). Deoxygenation was achieved by evacuating the sample with a vacuum pump and raising the pressure to 1 atm with purified N$_2$. Lactase concentration was $2.0 \times 10^{-4}$ M in 0.01 M phosphate buffer, pH 6.0. Illumination was 1400 lux. Each spectrum took 9 min to record. The solution was irradiated for 10 to 20 min between each spectrum (see inset). Inset, plot of log $A/A_0$ at 350 and 610 nm versus time, not counting the dark period necessary for recording (see text for justification of this assumption).
that we could not detect any change in the protein ultraviolet absorption band when care is taken not to excite this band ($\tau < 0.1\%$ at the wavelengths below 312 nm). Thus, the reversible spectral changes we observe do not cause irreversible damage to the aromatic side chains of the protein moiety.

DISCUSSION

The experiments reported here strongly suggest an energy transfer from the type 3 chromophore to type 1 copper. It is remarkable that when the protein is irradiated in the presence of oxygen this energy transfer from the type 3 to the type 1 site should be much faster (Fig. 7) than the speed of the type 3 chromophore reoxidation which is reported to be a fast process (19). Yet, the speed of photoreduction of the type 1 site is extremely slow.

It is known that the reoxidation by $O_2$ of type 1 and type 3 sites in chemically reduced lactase is extremely fast. Also the reoxidation of type 1 copper involves intramolecular transfer from the type 1 to the type 3 2-electron center. The kinetics that we observe differ by several orders of magnitude from those reported in the literature (2, 20) for the oxidation of the fully reduced protein, in which type 2 copper is also reduced. Our findings, therefore, lead us to suggest that the rate of the reoxidation process for fully reduced lactase depends upon the state of oxidation of type 2 copper.

The irradiation of ceruloplasmin or lactase causes the optical bleaching of the protein which is associated with the reduction of type 1 copper. Concomitant with this reduction, a new radical species is created. Reoxidation of the photoreduced protein either with $O_2$ or ferricyanide causes the reappearance of the radical. Some comments can be made on the nature of the radical induced by irradiation at 350 nm. Firstly, its anisotropy, $\Delta H_L = 85$ G, $\Delta H_T = 35$ G at 77 K (Fig. 3B) and $\Delta H_L = 82$ G, $\Delta H_T = 32$ G at 1.4 K, suggests that it is a biradical species (21). Secondly, the similar values of the splittings measured at 20°C ($\Delta H_L = 64$ G, $\Delta H_T = 29$ G) (Fig. 4C) indicate that irradiation induces the same biradical species on the protein at room temperature and in frozen solution. However, all our attempts to detect a $\Delta m = 2$ "forbidden" transition that is sometimes observed for biradicals (22) failed both at 77 K and 1.4 K. The signal we observe neither resembles that arising from nitric oxide-treated hemocyanin nor tyrosinase (23) where the splittings are much larger. If the four-line signal we observe is indeed that of a biradical, then the individual $S = \frac{1}{2}$ species that give rise to this signal must be much closer than in the NO-treated proteins (23).

The multiple reductions induced by irradiation raise the question of the source of electrons. As care was taken to remove Fe$^{3+}$ that can be a substrate for ceruloplasmin (24), there remain at least two candidates as electron donors, namely water or the carbohydrate moiety of the protein. Indeed, radicals similar to those reported here have been observed for γ-irradiated sugars (25, 26). Also, the oxidation of water by lactase is thermodynamically feasible (1, 2). While type 1 copper is not accessible to water (27), it is possible that type 3, the photoreduced species in our experiments, is accessible to the solvent. It is also possible that the carbohydrates are irreversibly oxidized, without affecting the reversibility of reduction of type 3 and type 1 centers. The bearing of these photochemical processes and energy transfer between sites on the functional properties of blue oxidases is presently being studied. Other copper proteins having different functions than the oxidases are also being investigated with respect to their photochemistry in order to test the specificity of the phenomena reported in this work.

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