

## AN ESR STUDY OF IRRADIATED MIXTURES OF HYDROGEN PEROXIDE AND Cu(II) COMPLEXES AT 77 K

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When aqueous solutions containing hydrogen peroxide and  $\text{CuSO}_4$  are irradiated by a high-pressure mercury lamp at room temperature and at 77 K, hydrogen peroxide decomposes and hydroxyl radicals generated in high concentrations coordinate to  $\text{CuSO}_4$ . The catalytic activity of Cu(II), which depends on the choice of the ligand (triene, diene, ethylenediamine, ammonia, EDTA, oxalic acid and glycerine) and the proportion between the monomeric and dimeric forms of the Cu(II) complex, shows a maximum at a concentration of  $10^{-4} \text{ mol dm}^{-3}$ . The catalytically active species is the monomeric Cu(II) complex, the dimer being inactive.

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Tkáč and his co-workers have demonstrated that interaction of t-butylhydroperoxide with cobalt(II) 2,4-pentanedionate in nonpolar solvents results in the formation of a radical of the type  $\text{ROO}\cdot$ , which coordinates to the cobalt atom and has a comparatively long lifetime<sup>1-3</sup>. This complex is a strong oxidizing agent, and has been used by the above workers to prepare many types of radical and for oxidation reactions<sup>4</sup>. In an attempt to find out an inorganic counterpart of the system in aqueous solution, we have studied the interaction of hydrogen peroxide with copper(II) sulfate with the aim to prepare a copper ion complex with radicals generated by hydrogen peroxide decomposition<sup>5</sup>.

The catalyzed decomposition of hydrogen peroxide has been studied frequently<sup>6-8</sup>, especially as a reaction involved in oxidations, hydroxylations and epoxidations by hydrogen peroxide. The course of the reaction has mostly been interpreted in terms of a free radical chain mechanism. Other explanations involve non-radical mechanisms<sup>8,9</sup>, mixed radical and non-radical mechanisms<sup>10,11</sup>, and parallel radical and non-radical decompositions<sup>12</sup>. Hydroxyl radicals formed by hydrogen peroxide decomposition have been found to exert a strong oxidative action<sup>13-15</sup>, and to form complexes, so extending their lifetime<sup>16,17</sup>.

Cu(II) complexes occur in solution predominantly as dimers<sup>18,19</sup>, whose spectra differ from those of monomeric Cu(II) complexes. The equilibrium concentration of the monomeric complex can be increased<sup>20</sup> by the addition of dimethyl sulfoxide (DMSO) or dimethylformamide (DMF). The monomer-to-dimer ratio may determine

the catalytic activity of the metal complex, or even the reaction mechanism, as has been observed for the system Fe(III)-EDTA-H<sub>2</sub>O<sub>2</sub><sup>1,2</sup>.

The aim of the present work was to ascertain what factors affect the generation of hydroxyl radicals by hydrogen peroxide decomposition in aqueous solution in the presence of copper(II) sulfate and the formation of complexes of the radicals with copper ions.

## EXPERIMENTAL

### Materials

The materials used were triethylenetetramine hydrochloride (triene) and diethylenetriamine (diene) of analytical grade (Koch and Light, Great Britain), a 30% aqueous solution of analytical grade hydrogen peroxide (8.82 mol dm<sup>-3</sup>), copper(II) sulfate pentahydrate of analytical grade, dimethyl sulfoxide and dimethylformamide of analytical grade, reagent grade glycerine, Na<sub>2</sub>EDTA of analytical grade, and Cu(II)EDTA (Lachema, Czechoslovakia).

### Instruments and Experimental Arrangement

ESR spectra were taken on an ERS-220 instrument (Academy of Sciences of the G.D.R.) operating in the X-band with a magnetic field modulation of 100 kHz. The magnetic field was measured with a Radiopan <sup>1</sup>H NMR magnetometer (Poland), and the microwave frequency was measured using a C3-54 frequency counter (U.S.S.R.). The calibration of the spin concentration was made with the aid of DPPH ( $g = 2.0037$ ) and Mn(II)/ZnS ( $g = 2.0024$ ,  $A = 64.00 \cdot 10^{-4} \text{ cm}^{-1}$ ) standards. The solutions were contained in flat quartz cells, where they formed layers 0.5 and 0.8 mm thick. The spectra at 77 K were measured using a quartz Dewar flask with a fingerlike projection placed in the resonator, and quartz tubular cells of 5 mm outer diameter and about 1 mm wall thickness. The samples were irradiated in the resonator by an HBO-200 high-pressure mercury lamp (Osram, F.R.G.). In some experiments, the radiation was filtered by band filters (Zeiss, G.D.R.).

### Procedures

The reaction mixtures were made up by rapidly mixing and homogenizing a CuSO<sub>4</sub> solution (with or without further components) and an aqueous solution of hydrogen peroxide. The operation took about 10 s. The mixtures placed in cells were frozen to 77 K by immersing the cells in liquid nitrogen in a Dewar flask. This operation was completed in about 15 s.

The free radical concentration was determined by measuring the signal height from a record in the form of the first derivative of the absorption signal and the signal width,  $\Delta H_{pp}$  (mT), and by matching them with signals of DPPH and Mn(II)/ZnS standards using a conventional procedure<sup>2,1</sup>.

## RESULTS

The radical generation was followed on irradiation at room temperature and the temperature of liquid nitrogen in the presence of ligands with different donor atoms.

### Experiments at Room Temperature

Solutions of hydrogen peroxide ( $1.00$  and  $8.82 \text{ mol dm}^{-3}$ ) were ESR inactive. An aqueous solution of copper(II) sulfate ( $1.00 \text{ mol dm}^{-3}$ ) gave an isotropic signal (singlet,  $g = 2.1958$ ,  $\Delta H_{pp} = 10.0 \text{ mT}$ ) arising from Cu(II) ions. On addition of hydrogen peroxide ( $1.00 \text{ mol dm}^{-3}$ ), this signal disappeared within 5 min, with simultaneous decomposition of hydrogen peroxide and liberation of oxygen. There was a redox change of Cu(II) ions, but it could not be definitely established whether the diamagnetic Cu(I) or Cu(III) ions were formed. When hydrogen peroxide had decomposed, the Cu(II) signal was restored to its original parameters. The redox change of Cu(II) also occurred at a  $\text{CuSO}_4$  concentration of  $1.00 \cdot 10^{-3} \text{ mol dm}^{-3}$  and an  $\text{H}_2\text{O}_2$  concentration of  $8.82 \text{ mol dm}^{-3}$ .

The addition of EDTA stabilizes Cu(II) by complexing it, and the decomposition of hydrogen peroxide proceeds with an induction period (of about 5 min) and at a substantially slower rate, again being associated with a redox change of Cu(II).

Solutions containing  $\text{CuSO}_4$  ( $1.00 \cdot 10^{-3} \text{ mol dm}^{-3}$ ), hydrogen peroxide ( $1.00 \text{ mol dm}^{-3}$ ), and an amine (triene, diene, or ethylenediamine, each in a concentration of  $1.00 \cdot 10^{-3} \text{ mol dm}^{-3}$ ) or ammonia ( $4 \cdot 10^{-3} \text{ mol dm}^{-3}$ ) give isotropic spectra of Cu(II) complexes with the amine, with a hyperfine splitting (quartet,  $S = 3/2$ ) which disappears within 20 min after mixing as a result of an interaction between Cu(II) and  $\text{H}_2\text{O}_2$ . Once all the hydrogen peroxide has reacted, Cu(II) is regenerated, but the spectra are associated with free Cu(II) ions. The reaction apparently involves an oxidative degradation of the Cu(II)-amine complex. In a solution containing Cu(II)EDTA ( $1.00 \cdot 10^{-3} \text{ mol dm}^{-3}$ ) and  $\text{H}_2\text{O}_2$  ( $1.00 \text{ mol dm}^{-3}$ ), the decomposition of hydrogen peroxide occurs only after an induction period (of about 5 min), and is very slow, once again being associated with removal of Cu(II) signal as a consequence of the Cu(II) redox change.

### Experiments at 77 K

A frozen aqueous solution of  $\text{CuSO}_4$  ( $1.00 \cdot 10^{-3} \text{ mol dm}^{-3}$ ) gives an anisotropic spectrum of the dimeric Cu(II) complex with an unresolved hyperfine structure; the  $g$ -factors depend on the concentration of  $\text{CuSO}_4$ , probably because aggregates of various degrees and structures are formed. The presence of DMSO ( $3.80 \text{ mol dm}^{-3}$ ) or DMF ( $3.80 \text{ mol dm}^{-3}$ ) gives rise to a spectrum with a hyperfine splitting in the parallel region (quartet,  $S = 3/2$ ) and an unresolved splitting in the perpendicular region of the spectrum. The spectrum of this type arises definitely from a monomeric Cu(II) complex with axial symmetry<sup>22</sup>. Irradiation of the above frozen solution of  $\text{CuSO}_4$  for 60 min produced no change in the ESR spectrum. A frozen solution containing  $\text{CuSO}_4$  ( $1.00 \cdot 10^{-3} \text{ mol dm}^{-3}$ ) and  $\text{H}_2\text{O}_2$  ( $1.00 \text{ mol dm}^{-3}$ ) also gives a spectrum with a hyperfine splitting in the parallel region and an unresolved splitting in the perpendicular region (see Table I), which arises from the monomeric Cu(II)

complex with axial symmetry. Thus, the addition of DMSO, DMF or  $\text{H}_2\text{O}_2$  shifts the dimer: monomer equilibrium well in favour of the monomeric  $\text{Cu(II)}$  complex.

Irradiation of a frozen solution containing  $\text{CuSO}_4$  ( $1.00 \cdot 10^{-3} \text{ mol dm}^{-3}$ ) and  $\text{H}_2\text{O}_2$  ( $1.00 \text{ mol dm}^{-3}$ ) in the resonator produces a radical which gives an isotropic signal (singlet,  $g = 2.0061$ ,  $\Delta H_{pp} = 3.50 \text{ mT}$ ). The concentration of the radical increases linearly with irradiation time (see Fig. 1). No changes in the spectrum of  $\text{Cu(II)}$  were observed over the period of irradiation.

### Effect of Ligands

We have studied the effects of amines (triene, diene, ethylenediamine, ammonia, and EDTA), oxalic acid and glycerine on the thermal and photochemical generation of radicals by hydrogen peroxide decomposition in the presence of  $\text{Cu(II)}$ . Irradiation of frozen solutions containing  $\text{CuSO}_4$  ( $1.00 \cdot 10^{-3} \text{ mol dm}^{-3}$ ),  $\text{H}_2\text{O}_2$  ( $1.00 \text{ mol dm}^{-3}$ ) and a ligand ( $1$  to  $4 \cdot 10^{-3} \text{ mol dm}^{-3}$ ) produced radicals giving an isotropic signal (singlet,  $g = 2.0061$ ,  $\Delta H_{pp} = 3.50 \text{ mT}$ ). The radical concentration increased linearly with irradiation time. The spectra and the parameters of the monomeric  $\text{Cu(II)}$  complexes are given in Table I. The bonding parameter  $\alpha^2$  indicates the character of the  $\text{Cu(II)}$ -ligand  $\sigma$ -bonding<sup>23</sup> ( $\alpha^2 = 1$  for ionic bonding, and  $\alpha^2 = 0.5$  for covalent bonding). Values of  $G \geq 4.00$  signify that the unpaired electron of  $\text{Cu(II)}$  is located in the  $d_{x^2-y^2}$  orbital<sup>24</sup>. As for the mixtures containing DMSO, a superposition of spectra of the monomeric and dimeric  $\text{Cu(II)}$  complexes was found for mixtures containing triene, diene, and ammonia (see Fig. 1). On heating the irradiated mixture

TABLE I

Parameters of ESR spectra of irradiated frozen  $\text{H}_2\text{O}_2$ - $\text{CuSO}_4$ -L mixtures at 77 K. L = ligand,  $[\text{H}_2\text{O}_2] = 1.00 \text{ mol dm}^{-3}$ ,  $[\text{Cu(II)}] = 1 \cdot 10^{-3} \text{ mol dm}^{-3}$ ; bonding parameter<sup>23</sup>  $\alpha^2 = A_{\text{iso}}/0.036 + (g_{\parallel} - 2.0032) + 3/7(g_{\perp} - 2.0032) + 0.04$ ; parameter<sup>24</sup>  $G = (g_{\parallel} - 2)/(g_{\perp} - 2)$

Ligand	[L]/[Cu]	$g_{\text{iso}}$	$A_{\text{iso}} \cdot 10^4 \text{ cm}^{-1}$	$g_{\parallel}$	$A_{\parallel} \cdot 10^4 \text{ cm}^{-1}$	$g_{\perp}$	$G$	$\alpha^2$
—	—	2.1848	48.72	2.3967	146.18	2.0789	5.028	0.873
Glycerine	1 368	2.1916	46.56	2.4131	139.69	2.0808	5.113	0.872
Triene	1	2.1881	48.57	2.4014	145.70	2.0815	4.925	0.878
Diene	1	2.1274	66.17	2.2262	198.51	2.0781	2.896	0.848
en	2	2.1258	61.84	2.2578	185.52	2.0598	4.311	0.835
en	1	2.1885	46.45	2.4074	139.36	2.0789	5.163	0.865
$\text{NH}_3$	4	2.1485	59.66	2.2369	178.97	2.1042	3.541	0.815
$(\text{COOH})_2$	1	2.1709	51.41	2.3600	154.22	2.0763	4.718	0.826
EDTA	1	2.1411	53.34	2.2866	160.01	2.0683	4.196	0.797

to room temperature, the signal of the radical disappeared (measured after repeated freezing to 77 K). The increase in the intensity of the spectra of the radicals generated is illustrated in Table II.

### Effect of Cu(II)EDTA

A frozen solution of CuEDTA ( $1 \cdot 10^{-3} \text{ mol dm}^{-3}$ ) gives an isotropic spectrum (singlet,  $g = 2.1278$ ,  $\Delta H_{pp} = 12.7 \text{ mT}$ ), as does a solution containing CuEDTA ( $1 \cdot 10^{-3} \text{ mol dm}^{-3}$ ) and  $\text{H}_2\text{O}_2$  ( $1.00 \cdot 10^{-2} \text{ mol dm}^{-3}$ ) (singlet,  $g = 2.1323$ ,  $\Delta H_{pp} = 14.0 \text{ mT}$ ). On increasing the concentration of  $\text{H}_2\text{O}_2$ , the frozen solution containing CuEDTA and  $\text{H}_2\text{O}_2$  gives an anisotropic spectrum of Cu(II) with a hyperfine splitting in the parallel region of the spectrum ( $g_{\parallel} = 2.2004$ ,  $A_{\parallel} = 160.30 \cdot 10^{-4} \text{ cm}^{-1}$ ,  $g_{\perp} = 2.0007$ ). Irradiation generates a radical that gives an isotropic signal (singlet,  $g = 2.0071$ ,  $\Delta H_{pp} = 1.50 \text{ mT}$ ). The intensity of the signal increases linearly with irradiation time. No changes in the spectrum of Cu(II) were observed over the period of irradiation. For systems with large values of  $a$  (triene and diene, see Table II), radicals were detected even in the absence of irradiation; these radicals were generated

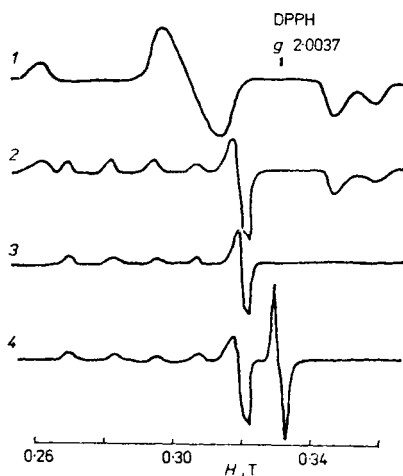


FIG. 1

ESR spectra of frozen aqueous solutions of  $\text{CuSO}_4$  ( $1 \cdot 10^{-3} \text{ mol dm}^{-3}$ ) at 77 K. Microwave power, 20 mW; modulation amplitude, 0.5 mT; attenuation, 30 dB; response time, 0.2 s; chart speed,  $7.7 \text{ mT min}^{-1}$ . 1 Spectrum of dimeric Cu(II) complex; 2  $[\text{DMSO}] = 3.80 \text{ mol dm}^{-3}$ , superposition of spectra of monomeric and dimeric Cu(II) complexes; 3  $[\text{H}_2\text{O}_2] = 1.00 \text{ mol dm}^{-3}$ , spectrum of monomeric Cu(II) complex; 4 spectrum of the same mixture: on irradiation by a mercury lamp a signal of hydroxyl radical appears in the region 0.33 T

by the thermal reaction at room temperature, and were stabilized by rapid freezing to 77 K.

### Effect of Cu(II) Concentration on Radical Generation

The photochemical generation of radicals depends on the concentration of  $\text{CuSO}_4$  in the way illustrated in Fig. 2. At Cu(II) concentrations higher than  $1 \cdot 10^{-4}$  mol  $\text{dm}^{-3}$ , the spectrum of the monomeric Cu(II) complex with axial symmetry

TABLE II

Increase in the hydroxyl radical concentration, measured as the intensity (height) of OH $\cdot$  signal (cm), with irradiation time  $t$  (min).  $v = a + bt$ ;  $a, b =$  coefficients,  $[\text{H}_2\text{O}_2] = 1.00$  mol  $\text{dm}^{-3}$ ,  $[\text{Cu(II)}] = 1 \cdot 10^{-3}$  mol  $\text{dm}^{-3}$ , L = ligand

Ligand	[L]/[Cu(II)]	$a$	$b$
—	—	0	0.3490
Glycerine	1 368	0	0.1536
Triene	1	4.300	0.0933
Diene	1	15.400	0.0707
en	2	2.000	0.0513
en	1	1.500	0.0873
NH <sub>3</sub>	4	0.100	0.0331
EDTA	1	0	0.0024

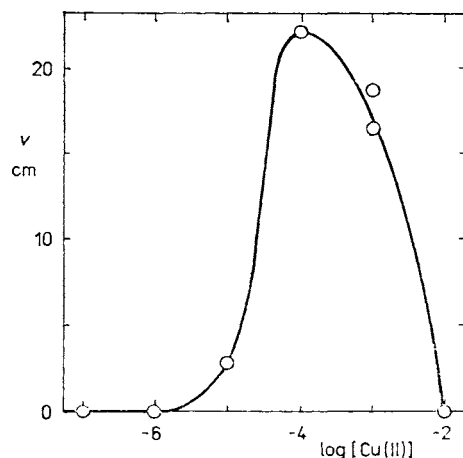


FIG. 2

Dependence of the hydroxyl radical concentration, measured as the intensity (height) of ESR signal, on the concentration of  $\text{CuSO}_4$ . Temperature, 77 K;  $[\text{H}_2\text{O}_2] = 1.00$  mol  $\text{dm}^{-3}$ ; irradiation time, 60 min. Conditions of the ESR measurements are as in Fig. 1

becomes weaker, while the spectrum of the dimer increases in intensity. This implies that it is the monomeric Cu(II) complex that is active in catalyzing the decomposition of hydrogen peroxide.

#### *Effect of Light Filtration on Radical Generation*

The above results refer to irradiation of frozen solutions containing  $\text{CuSO}_4$  and  $\text{H}_2\text{O}_2$  by the full output of the mercury lamp. Next, we used band filters and studied the effect of the wavelength of the incident radiation on radical generation. Compared with unfiltered radiation (100%), the quantity of radicals generated in the system with  $\text{CuSO}_4$  ( $1 \cdot 10^{-3} \text{ mol dm}^{-3}$ ) and  $\text{H}_2\text{O}_2$  ( $1.00 \text{ mol dm}^{-3}$ ) over the same period of irradiation (60 min) falls down to 4.8% for a filter transmitting light of wavelengths in the region 320 to 400 nm, to 1.3% for the region 660 to 890 nm, and to zero for the region 480 to 570 nm. According to the literature<sup>25</sup>, hydrogen peroxide absorbs light of wavelengths in the region below 400 nm, the absorption being especially strong below 300 nm.

#### *Check and Comparative Experiments*

By irradiating frozen solutions of hydrogen peroxide ( $1.00$  and  $8.82 \text{ mol dm}^{-3}$ ), anisotropic spectra typical of superoxide radicals ( $g_{\parallel} = 2.0306$ ,  $g_{\perp} = 2.0058$ ) were obtained. The intensity of the spectra increased very slowly with irradiation time. The spectra required a minimum of 120 min irradiation to develop. This result is taken as representing uncatalyzed decomposition of hydrogen peroxide. The spectra of the photochemically generated superoxide radicals were compared with those observed for superoxide radicals generated thermally at room temperature by hydrogen peroxide decomposition in solution with added NaOH ( $g_{\parallel} = 2.0659$ ,  $g_{\perp} = 2.0080$ ). When this mixture is irradiated at 77 K, the intensity of its spectrum increases linearly with irradiation time. The difference in the values of  $g_{\parallel}$  may be due to interactions of the radicals with different matrices and to different freezing modes<sup>26,27</sup>.

## DISCUSSION

Copper(II) sulfate forms predominantly dimeric complexes, and probably also higher aggregates, in aqueous solutions. The addition of DMSO or DMF shifts the monomer:dimer equilibrium well in favour of the monomer, as a result of the formation of a complex of DMSO or DMF with the monomeric Cu(II) complex. Hydrogen peroxide at a concentration of  $1.00 \text{ mol dm}^{-3}$  and higher has the same effect, as indicated by the hyperfine splitting in the parallel region of the spectra. Spectra of this type are associated with monomeric Cu(II) complexes with axial symmetry<sup>22</sup>. The formation of a complex of hydrogen peroxide with Cu(II) ions

has been described in the literature<sup>28</sup>. The experiments with filtered radiation indicate that the complex of Cu(II) with H<sub>2</sub>O<sub>2</sub> absorbs radiation of wavelengths shorter than 320 nm.

Irradiation of the Cu(II)-H<sub>2</sub>O<sub>2</sub> complex at 77 K gives rise to a radical which vanishes at room temperature. According to the literature<sup>29</sup>, irradiation of frozen solutions without any added metal complex generates an isotropic signal due to the HO<sub>2</sub><sup>•</sup> or O<sub>3</sub><sup>-•</sup> radical. In the presence of Cu(II) ions, the hydroxyl radical probably coordinates more readily to copper atoms than to oxygen also present in the mixture as a result of thermal decomposition of hydrogen peroxide at room temperature and diffusion from the air to the solution. The bonding to copper extends the lifetime of the hydroxyl radical, making it possible to obtain its spectrum by rapid freezing of Cu(II)-H<sub>2</sub>O<sub>2</sub> mixtures containing diene or triene. The hydroxyl radicals are also generated in solution by thermal decomposition of hydrogen peroxide at room temperature in the presence of Ti(III) ions<sup>16,17</sup>; here, a Ti(IV)-OH complex has been shown to be formed. Unless the OH<sup>•</sup>, O<sub>3</sub>H<sup>•</sup> or O<sub>3</sub><sup>-•</sup> free radicals are stabilized by coordination to copper atoms, they react with the ligands of the complexes or enter into a competitive reaction to yield superoxide radicals, which have been shown to form in both the thermal and photochemical reactions of hydrogen peroxide in the absence of CuSO<sub>4</sub>.

At higher CuSO<sub>4</sub> concentrations (above 1 · 10<sup>-4</sup> mol dm<sup>-3</sup>), the catalytic activity of Cu(II) decreases as a result of an increase in the concentration of the catalytically inactive Cu(II) complex. No definite conclusion can be made as to whether Cu(I) or Cu(III) results from the redox change of Cu(II), since ESR measurements do not permit an assignment to be made, and there are many conflicting statements in the literature on the subject.

It may be concluded that the first step in both the thermal and photochemical decomposition of hydrogen peroxide catalyzed by the above complex of Cu(II) is the formation of a Cu(II)-H<sub>2</sub>O<sub>2</sub> complex in which hydrogen peroxide is broken up into hydroxyl radicals. The overall mechanism involves an association followed by a radical reaction. It is believed that this finding may reconcile the extreme proposals in which either a purely radical or a purely non-radical mechanism of the reaction is considered.

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