Evidence for a Two Step-One Electron Mechanism in the Heterogeneous Catalytic Decomposition of Hydrogen Peroxide by Copper(II)-Peroxide

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Only very little is known in detail on the mechanism of the heterogeneous catalytic decomposition of H_2O_2[1,2]. This process can be regarded as an oxidation of H_2O_2 to the stage of oxygen. Among various compounds copper(II)-hydroxide in colloidal solution and in suspension was found to be catalytically active[1]. Since $Cu(OH)_2$ reacts with H_2O_2 under formation of copper peroxide compounds[3-7], it has been argued[1,6,8] that these compounds are involved in H_2O_2 decomposition. But nothing is known on the mechanism of this process. The EPR investigations reported here yield evidence that the oxidation of H_2O_2 by the copper peroxide precipitate has to be described by a two step-one electron transfer mechanism involving HO_2 and HO radicals as intermediate products.

Copper hydroxide may be prepared by precipitation from solutions of a copper(II)-salt using excess amounts of alkali at temperatures below 5 °C[3,9,10]. Then an excess amount of conc. H_2O_2 (11 M) was dropped to the copper hydroxide suspension which results in the formation of dark brown copper(II) peroxide [*e.g.*[3-7]]. An intensive O_2 evolution set in immediately. The suspended precipitate was transferred to the EPR sample tube and frozen at 77 °K. This sample only showed the intensive signal with axial symmetry represented on Fig. 1. In a second experiment the copper peroxide precipitate was filtered off, immediately transferred to the sample tube, resuspended in methanol, and suddenly frozen at 77 °K. In addition to the strong signal a weaker three line spectrum appeared (Fig. 1).

The EPR spectra were recorded by the Varian E–12 spectrometer under usual conditions. All chemicals used were of analytical grade. Only trace amounts of heavy metals were present which cannot account for the intensive effects observed.

With the simple freezing method described above the existence of at least three unstable intermediate reaction products formed during the heterogeneous catalytic decomposition of H_2O_2 in alkaline $Cu(OH)_2$-suspensions has been established which will now be discussed in some detail.

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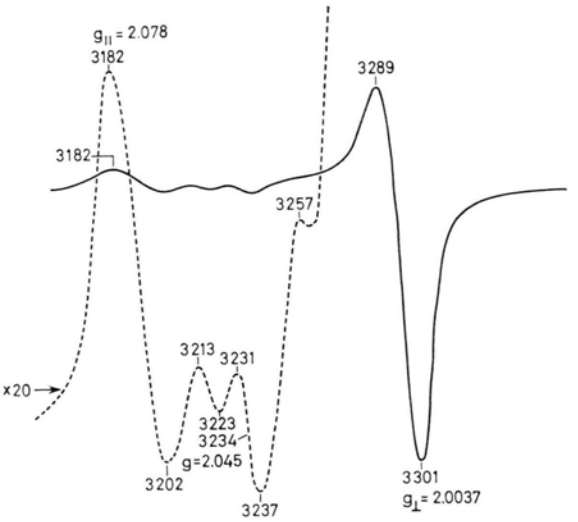

Fig. 1. EPR spectrum of an alkaline suspension of copper hydroxide in methanol and H_2O_2 at the beginning of oxygen evolution. Mole ratio $H_2O_2/Cu(OH)_2$ = 100; 0,2 M KOH, modulation amplitude: 2 G, microwave power: 200 mW, temperature: 93 °K, DPPH: 14,0534 MHz.

1. The EPR spectrum of the copper peroxide precipitate in methanol at 90 °K reveals the formation of two radical species (Fig. 1). The intensive signal with axial symmetry can be attributed to the O_2^- radical trapped in methanol. The *g* values were found to be in agreement with those obtained by BENNETT *et. al.*[11] in pure methanol within experimental error. This shows that O_2^- is not complexed with copper or adsorbed on the surface of copper peroxide. The demonstration of O_2^- as a precursor of O_2 reveals that the decomposition of H_2O_2 by copper peroxide occurs *via* a *two step-one electron mechanism*.

No EPR signal due to a copper(III)-compound could be observed the formation of which is highly improbable anyway because of the low oxidation potential of H_2O_2 in strongly alkaline solutions[12]. Hence, we must conclude that it is the HO_2 radical which is primarily generated. Because of its pK-value of 4,5[13,14] it dissociates in alkaline solutions into O_2^- and H^+.

2. The weak three-line signal with the line splittings of 16 G and 15 G (after correction for the superposition of the third line on the $g_{\perp}$-absorption of O_2^-) is identified with the CH_2OH radical. The intensity ratio of the three lines was found to be approx. 1 : 2.3 : 1.2 (Fig. 1) which is fairly consistent with the theoretical value expected for CH_2OH. The *g*-value of the radical observed in the suspension

($g = 2{,}045$), however, differs from that obtained in a homogeneous solution which was determined to be 2,001[15]. Presumably the radicals are adsorbed on the surface of the solid copper peroxide precipitate. Thus the highly reactive CH_2OH radical is stabilized to some extent. This would account for its detection by the rather slow freezing technique applied. The formation of the CH_2OH radical implies the *generation of OH as a secondary radical* by the reaction of HO_2 with H_2O_2, since HO_2 does not react directly with methanol[16,17].

3. In alkaline suspensions of freshly precipitated copper peroxide *no EPR signal due to a copper(II)-compound* was found at the beginning of O_2 evolution in the range 0–11000 G. This result can be most readily explained on the assumption that a diamagnetic copper(I)-compound has been formed[18]. This would be consistent with the view that primarily HO_2 radicals are formed.

But during the course of the O_2 evolution an intensive signal at $g = 2{,}173$ ($\Delta H_{1/2} = 182$ G) appeared together with the O_2^- spectrum (Fig. 2). It is not identical with that of $Cu(OH)_2$, or copper(II)-peroxide, or CuO either[18].

It has been also observed, however, in alkaline $Cu(OH)_2$ suspensions which had been aged for four days at 4 °C and in a copper peroxide powder sample (mole ratio $H_2O_2/Cu(OH)_2 = 1$) after glowing. This indicates that the unknown signal must be related to a specially structured copper(II)-hydroxide or to a decomposition product of it which may be also formed on copper(II) peroxide decomposition.

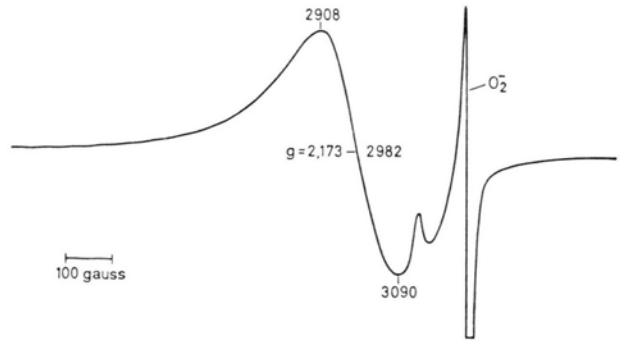

Fig. 2. EPR spectrum of the same suspension during the course of oxygen evolution. Modulation amplitude: 10 G, microwave power: 200 mW, microwave frequency: 9,069143 GHz, temperature: 93 °K.

After cessation of O_2 evolution the signal at $g = 2{,}173$ disappeared.

These observations demonstrate that the decomposition of H_2O_2 is accompanied by a *reversible* decomposition of the catalytically active copper compound.

The EPR results are clearly incompatible with the view that O_2 evolution is simply caused by a decay of copper peroxide under formation of CuO.

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