The Mechanism of Hydrogen Peroxide Bleaching

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Hydrogen peroxide is finding increasing application as the preferred bleaching agent in both industrial and domestic situations. There is general acceptance that it acts by destructively oxidizing the colored organic molecules involved, but the mechanism of such oxidation is still being debated.

Previous Work

Dannacher and Schlenker have recently elaborated their earlier work on the peroxide bleaching of tea-stained cotton fabrics at 60C in alkaline buffers.[1,2] By the use of trap tests and other experiments, they ruled out singlet oxygen and the hydroxyl radical $HO^{\bullet}$ as the active oxygen species responsible, but suggested that the active agent was the perhydroxyl radical $HO_2^{\bullet}$ formed by the disproportionation reaction:

$$HO_2^- + H_2O_2 \rightarrow HO_2^{\bullet} + HO^- + HO^{\bullet} \quad \text{Eq. 1}$$

In alkaline media $HO_2^{\bullet}$ largely dissociated to the superoxide radical $O_2^{-\bullet}$. By also considering the reactions of $HO^{\bullet}$ and $HO_2^{\bullet}$ with H_2O_2 and the three chain-breaking reactions by combinations of radicals, Dannacher and Schlenker estimated that the stationary concentration of $O_2^{-\bullet}$ was given by:

$$\left[O_2^{-\bullet}\right] \propto \sqrt{A \times \left[H_2O_2\right] \times \left[HO_2^-\right]} \quad \text{Eq. 2}$$

where *A* was a complex but not explicitly stated function of the various rate and equilibrium constants involved and of pH. A plot of the calculated superoxide concentration against pH gave a maximum at about pH 10.8, as did a plot of the experimentally obtained first-order rate constants for tea-stain bleaching.

Superoxide Radical

Dannacher and Schlenker concluded that $O_2^{-\bullet}$ was the active agent involved in bleaching the tea chromophoric system. However, tea stains are complex mixtures of colored polyphenolic compounds with unknown protonation constants.[3,4] Kinetic investigations of peroxide bleaching are more easily interpreted using single colored compounds with known properties. It is therefore interesting that Dannacher and Schlenker's finding[1,2] of a maximum bleaching rate at 60C at pH 10.8 is similar to the results in a paper by Ohura et al. which they do not quote.[5] Ohura et al. obtained maximum rate constants at pH 11-11.5 in bleaching by peroxocarbonate (which dissociates to H_2O_2 in solution)[6] of several colorants in aqueous solution at 20C, but they did not interpret their results mechanistically.

Work with Single Colorants

We have obtained rather different results in a series of kinetic studies[7-10] that were not referred to by Dannacher and Schlenker. The rates of bleaching by hydrogen peroxide of phenolphthalein,[7,8] alizarin,[9] and crocetin[9] were measured spectrophotometrically over an alkaline pH range at 21C or 25C and found always to be first order in colorant and first order in hydrogen peroxide. The second order rate constants for phenolphthalein rose steadily with increasing pH over the range 9-14 and for alizarin and crocetin from 10-12, with no maximum at around pH 11. None of the rates was affected by adding the trapping agent *N*-tert-butyl-α-phenylnitrone[11] which ruled out $HO^{\bullet}$ and $HO_2^{\bullet}$ as the active agents. Singlet oxygen played no appreciable role either, as shown by the absence of any effect on adding the trapping agent 2,5-dimethylfuran or by changing the solvent to 50 vol% D_2O in which the lifetime of single oxygen is greatly increased.[12] In fact all the kinetic data could be accounted for quantitatively on the premise that HO_2^- and H_2O_2 were the only active oxidizing species of the various protonated and deprotonated colorant species. Rate constants so derived (Table I) showed that for phenolphthalein and crocetin, the perhydroxyl ion was a more powerful oxidant than the H_2O_2 molecule. At sufficiently high pH, the bleaching largely occurs between HO_2^- and the most deprotonated form of the colorant while, at sufficiently low pH, the predominant reaction is between the H_2O_2 molecule and the protonated colorant. Hence plots of rate constant versus pH take on distorted S-shapes, as with phenolphthalein and crocetin. For alizarin (H_2Az), however, the bleaching rate constant reached a maximum around pH 12 and was then predicted to decrease to a lower plateau value at still higher pH because the HO_2^- ion attacks the HAz^- ion more rapidly than the fully deprotonated Az^{-2} ion.

Table I. Rate Constant Summary

Colorant Species	Temperature (C)	$k_2/10^{-3}$ (L/mol s) HO_2^-	H_2O_2
Phenolphthalein^{-2}	21	156	≤ 1.7
Alizarin^{-2}	21	1.3	--
Crocetin^{-2}	25	3.9	0.26
Malvin^{+}	25	--	39.5

In the case of malvin chloride, whose bleaching was studied over the lower pH range of 1.5-4.0, the only significant oxidant was the H_2O_2 molecule.[10] This species is therefore not as inert as Dannacher and Schlenker believed.[1] The evidence of all the above experiments shows that in peroxide bleaching of a wide range of colorants there is no need to invoke any oxidizing species other than HO_2^- and H_2O_2.

Singlet Oxygen

Neither Dannacher and Schlenker[1] nor Ohura et al.[5] added any chelating agent to the bleach solution. However, we found it essential[9] to add low concentrations of the transition-metal sequestering agent Dequest 2060 to the experiments with alizarin and crocetin because the rates of bleaching and peroxide decomposition were increased by the presence of metal impurities. In fact, certain metal compounds can change not only the rates but also the mechanisms. Thus, when significant amounts of molybdate or tungstate ions were added in the peroxide bleaching of phenolphthalein, a new form of catalysis appeared which was caused by the production of singlet oxygen.[13] It is relevant to add that tea stains are likely to include manganese and other metal ions.[14]

Conclusion

We conclude that the main oxidizing species in uncatalysed hydrogen peroxide bleaching of many colorants are just the H_2O_2 molecule itself (at lower pH) and the HO_2^- ion (at higher pH).

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