Mechanism of Peroxide Bleaching at High pH

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The peroxide bleaching of aqueous phenolphthalein, alizarin and crocetin in alkaline solution is not caused by free radical species, nor by singlet oxygen, but by hydrogen peroxide and the perhydroxyl anion, HOO^-.

Bleaching by hydrogen peroxide occurs as a result of the destructive oxidation of coloured organic molecules. The process is of special interest in alkaline media in which industrial and domestic bleaching is carried out. However, despite several published studies, the mechanism of alkaline peroxide bleaching is still in doubt, with several different oxidising species having been suggested. We have recently carried out kinetic studies of the peroxide bleaching of several organic colouring agents, which show how these points can be resolved.

Reaction mixtures were prepared in buffered aqueous solutions, over the pH range 9 to 12. Reactions were followed spectrophotometrically, at constant temperature, by measuring the decay in absorbance of the absorbance maximum of the colourant as a function of time. Typical reactant concentrations were 3×10^{-5} mol dm^{-3} in the colourant and 1×10^{-3} to 1×10^{-2} mol dm^{-3} in hydrogen peroxide.

Davies *et al.*,[1] Taher *et al.*,[2] and, more recently, Dannacher *et al.*[3] have proposed free radicals such as HO·, HOO· and $O_2^{-\bullet}$ as key species involved in the bleaching mechanism.

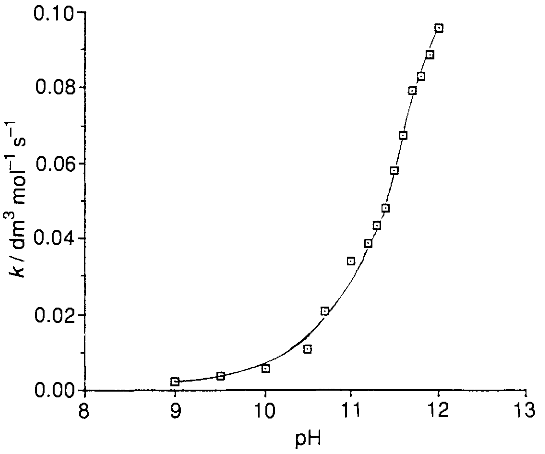

Fig. 1 Plot of second-order rate constant against pH for the reaction between aqueous phenolphthalein and hydrogen peroxide at 21.0 °C

However, as Table 1 shows we found that addition of the free radical trap *N*-*tert*-butyl-α-phenylnitrone[4,5] (5×10^{-4} mol dm^{-3}) to each of the phenolphthalein, alizarin and crocetin–hydrogen peroxide mixtures at pH 10 had no effect on the rates of reaction.

Another active bleaching species suggested in the literature[6] is singlet oxygen, $^1O_2$. This was tested for each of the above systems by the addition of the $^1O_2$ trap 2,5-dimethylfuran[7] (4×10^{-3} mol dm^{-3}) at pH 10.0. Again, Table 1 shows that no changes in the bleaching rates were observed. Additionally, there was no significant change in the rate of bleaching of phenolphthalein when carried out in 50 vol% D_2O, although the lifetime of $^1O_2$ is greatly increased by solvent deuteriation.[7,8] Moreover, in an experiment carried out with the addition of potassium molybdate (2×10^{-3} mol dm^{-3}), which enhances the rate of bleaching of phenolphthalein, introduction of 2,5-dimethylfuran largely eroded this increase (by 76%, at a hydrogen peroxide concentration of 0.01 mol dm^{-3}). Singlet oxygen is known to be formed by decomposition of peroxomolybdate complexes,[9] and the above result indicates that it makes a significant contribution to bleaching in the molybdate system. We conclude that $^1O_2$ plays no significant role in bleaching by hydrogen peroxide alone, which confirms the conclusion reached by Koberstein *et al.*[10] in their study of the peroxide bleaching of 1,3-diphenylisobenzofuran.

Another phenomenon found by several authors[2,6] is that the rate of bleaching by hydrogen peroxide passes through a maximum at high pH, within the range 9–12. Many of these studies involved stains absorbed onto a fabric, where the decrease in rate at very high pH can be explained by the greater repulsion between the negatively charged fabric and the increased proportion of HO_2^- anions present. Quite recently, however, Ohura *et al.*[11] have reported maxima in the rate constants at around pH 11 in the bleaching by 'peroxocarbonate', which dissociates to hydrogen peroxide in solution,[12] of several colourants in aqueous solution. This resembles the behaviour of the 'spontaneous' decomposition of hydrogen peroxide, ascribed to a bimolecular reaction between H_2O_2 molecules and HO_2^- anions.[13] Our experiments with phenolphthalein, alizarin and crocetin have shown, however, that the bleaching reaction is always first order in total peroxide as well as first order in the organic substrate. Moreover, the second-order rate constants, k, rise steeply and monotonically at high pH, with no sign of any maximum. The results for phenolphthalein are presented in Fig. 1, where the curve is seen to pass smoothly through the pH regions where phenolphthalein ($pK_1 = 9.0_7$, $pK_2 = 9.5_6$)[14] and hydrogen peroxide ($pK_a = 11.7_3$)[15] dissociate.

Table 1 Comparison of rates of oxidation by hydrogen peroxide in the presence and absence of free radical and singlet oxygen trapping agents, at pH 10 at 21.0 °C

Colourant	Rate constant in absence of trapping agents/ 10^{-4} dm^3 mol^{-1} s^{-1}	Rate constant in presence of radical trap/ 10^{-4} dm^3 mol^{-1} s^{-1}	Rate constant in presence of singlet oxygen trap/10^{-4} mol dm^3 s^{-1}
Phenolphthalein	54.4 54.0[a]	55.7	53.9
Alizarin	2.78	2.72	2.84
Crocetin at 25.0 °C	3.97	4.05	3.91

[a] In 50 vol% D_2O as solvent.

A detailed analysis of the results shows that the curve can be quantitatively understood in terms of reactions between the various forms of both phenolphthalein and hydrogen peroxide present in alkaline solution,[16] the highest rate constant being obtained for the reaction between the doubly ionised bisphenolic form of phenolphthalein and the HO_2^- anion. The overall rate constant should, therefore, ultimately reach a plateau value at very high pH. However, in order to obtain reproducible results for the experiments at these high pH values it was found necessary to add the polyphosphate metal-sequestering agent, Dequest 2060, to minimise peroxide decomposition. It may well be that the maxima reported in the literature were due to this undesirable side reaction.

To summarise, we have found no evidence for the participation of either free radicals or singlet oxygen in the alkaline bleaching of phenolphthalein, crocetin and alizarin by hydrogen peroxide. Nor was there any sign of the bleaching rate passing through a maximum at high pH. We strongly recommend for future work the use of the appropriate trapping agents (or, for singlet oxygen, the measurement of IR phosphorescence[17]) and the addition of a metal-sequestering agent in all kinetic studies with alkaline peroxide solutions.

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