The Formation and Radical Scavenging Properties of Ethylenediaminetetra-acetic Acid *N,N'*-Dioxide in Aqueous *m*-Chloroperbenzoic Acid

D. Martin Davies,* David Dunn, Mohammad Haydarali, Roland M. Jones, and J. Mark Lawther

School of Chemical and Life Sciences, Newcastle upon Tyne Polytechnic, Newcastle upon Tyne NE1 8ST, U.K.

meta-Chloroperbenzoic acid rapidly oxidizes ethylenediaminetetra-acetic acid to the *N,N'*-dioxide which suppresses the Cu^{II} catalysed *m*-chloroperbenzoic acid oxidation of amaranth [trisodium 1-(4-sulpho-1-naphthylazo)-2-naphthol-3,6-disulphonate] by scavenging free radical chain propagating species.

It is well-known that chelating agents inhibit metal-ion-catalysed reactions of hydroperoxides by hindering co-ordination of the hydroperoxide to the metal and also by preventing electron transfer to give free radicals by stabilizing one oxidation state of the metal.[1] We report here that edta (H_4edta = ethylenediaminetetra-acetic acid) added to solutions of *m*-chloroperbenzoic acid (MCPBA) inhibits a metal-ion-catalysed reaction not by chelating the metal ion but by forming edta *N,N'*-dioxide which scavenges radical chain-propagators.

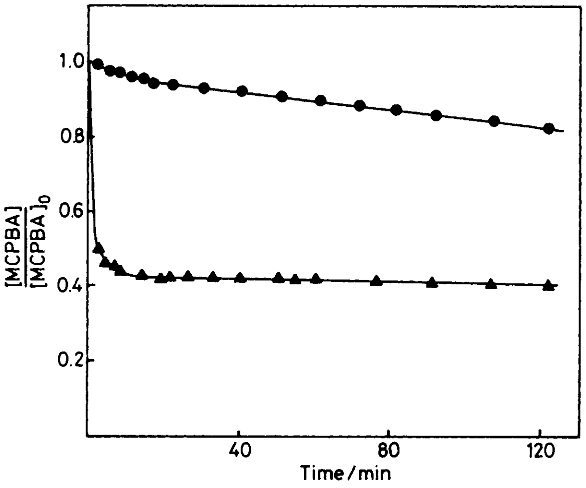

Figure 1. Reaction of *ca.* 3.5×10^{-3} M MCPBA with 1×10^{-3} M edta, ▲; and Cu^{II} edta, ●; at 25 °C, pH 6.6 ± 0.1, ionic strengh 0.1 (phosphate buffer).

Table 1. Dependence of duration of suppression on the volume of saturated 2-t-butyl-4-methoxyphenol solution added to 3 ml of a reaction solution with $[Cu^{II}] = 4.95 \times 10^{-5}$, [amaranth] = 2.88×10^{-5}, and [MCPBA] = 1×10^{-3} M in pH 6.5 phosphate buffer (I = 0.1) at 25 °C.

Volume/μl	Duration/s
1	53
3	101
5	152
10	203

Table 2. Initial rate as a function of [edta *N,N'*-dioxide] for the MCPBA oxidation of amaranth catalysed by 4.95×10^{-5} M Cu^{II}, conditions as Table 1: see text for experimental procedures.

10^6[edta *N,N'*-dioxide]/M	10^3 Initial rate[a]/$cm^{-1} s^{-1}$
0	15.2
1.0	2.60
2.0	2.04
4.0	1.81
10.0	1.37
20.0	0.93

[a] Absorbance change at 522 nm.

Figure 1 shows that unco-ordinated edta, but not Cu^{II} edta reacts rapidly with MCPBA. The stoicheiometry is one mole edta plus two moles MCPBA. Metal ions also stabilize edta with respect to alkaline ferricyanide oxidation.[2] MCPBA (2.5 g) and Na_2H_2edta (2 g) were stirred with 43 ml of 2.2% w/v aqueous NaOH at room temperature and the resulting solution was acidified with 2.5 ml sulphuric acid to give a white precipitate which was washed with water and with ethanol. The product (yield 80%) decomposes at 154 °C; elemental analysis is consistent with edta *N,N'*-dioxide·$\frac{1}{2}H_2O$.

The oxidation of amaranth [amaranth = trisodium 1-(4-sulpho-1-naphthylazo)-2-naphthol-3,6-disulphonate] with substituted perbenzoic acids is suppressed by the addition of edta which implies that a trace metal catalysed pathway exists.[3] The Cu^{II} catalysed MCPBA oxidation of amaranth was monitored spectrophotometrically at the absorbance maximum of the dye, 522 nm. Table 1 shows that a small volume of a saturated solution of the radical scavenger 2-t-butyl-4-methoxyphenol added during the course of the reaction suppresses the oxidation for a period of time which is dependent on the volume added. This suppression of the Cu^{II} catalysed oxidation indicates that the reaction is a radical chain process. The rate of the Cu^{II} catalysed MCPBA oxidation of amaranth is also reduced when edta is added during the course of the reaction (results not shown). The edta either chelates the Cu^{II} and reduces its catalytic activity or is oxidized by the peracid to the *N,N'*-dioxide which inhibits the oxidation reaction. The latter possibility was tested as follows. Stock solutions of amaranth, edta *N,N'*-dioxide if required, and copper sulphate were added in sequence to buffer and allowed to equilibrate for two hours at 25 °C before adding the peracid solution to start the reaction. Table 2 shows that the reaction is suppressed with a small concentration of edta *N,N'*-dioxide relative to the Cu^{II} concentration. The edta *N,N'*-dioxide cannot bind all of the Cu^{II}, neither does it bind all of an active form of the Cu^{II} (with the remaining Cu^{II} in the form of inactive Cu^{II} phosphate complexes) since the Cu^{II} species were allowed to equilibrate before the reaction was started. It is possible that the edta *N,N'*-dioxide binds a trace metal ion which acts synergistically with Cu^{II} and thus inhibits the Cu^{II} catalysed reaction. The explanation which we favour, however, is that edta *N,N'*-dioxide acts as a chain-breaker and scavenges chain-propagating species in the Cu^{II} catalysed MCPBA oxidation of amaranth.

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