

ABSTRACT

In recent years, organic peroxy acids have been reported to have utility in oral care products as disinfecting and tooth whitening agents. The use of such compounds in toothpastes or mouthrinses will inevitably lead to some ingestion by the consumers. Because of the reactive nature of the peroxy acids, we undertook an investigation to determine the fate of magnesium monoperoxyphthalate (MMPP) under simulated gastric conditions. The acidic pH coupled with the presence of ubiquitous chloride ion has led to rapid oxidation of chloride to chlorine by MMPP and the chlorine or hypochlorous acid thus formed reacted rapidly with a second molecule of MMP resulting in the formation of singlet oxygen. Singlet oxygen was detected by luminescence spectroscopy by measuring its emission at 1268 nm in a mixed solvent containing D₂O/H₂O. Absolute confirmation for the formation of singlet oxygen was made by comparing the luminescence decay rates in the MMPP reaction with those of a known reaction involving N-chlorosuccinimide (NCS) and hydrogen peroxide. **It is concluded that the reaction of MMPP with chloride ion at low pH produces singlet oxygen with high efficiency. The kinetics are consistent with a rate determining oxidation of chloride ion to hypochlorous acid, followed by reaction of the resulting hypochlorous acid with the peroxy acid to produce singlet oxygen in nearly quantitative yield.**

INTRODUCTION

The thermal decomposition of peroxyacids in aqueous solutions to form the parent acid and oxygen has been extensively investigated. In all cases, the rate of peroxyacid decomposition is second order in total peroxide concentration, with the maximum rate occurring at a pH equal to the pK of the peroxyacid. These results are consistent with a mechanism involving nucleophilic attack by the peroxyacid anion on the undissociated peroxyacid. Several reports have confirmed that this reaction produces singlet molecular oxygen in high yield. Since the pK values of most peroxyacids lie between 7 and 10, these studies have been limited to alkaline solutions.

This paper describes the results of our investigation of the reaction of magnesium monoperoxyphthalate hexahydrate (MMPP) with chloride ion in acidic medium (pH 2-5). A mechanism is proposed on the basis of the experimentally observed rate behavior.

OBJECTIVE

In recent years, organic peroxyacids have been reported to have utility in oral care products as disinfecting and tooth whitening agents. Because of the reactive nature of the peroxyacids, we undertook an investigation to determine the fate of MMPP under simulated gastric conditions as the possibility for ingestion is high with any oral use product.

MATERIALS AND METHODS

MMPP was purchased from Aldrich Chemical Co.; its iodometric purity was 86.6%. The apparatus for detection of singlet oxygen contained a thermostated glass cuvette, an optical chopper working at 100 Hz, a 0.25 M monochromator with 200 nm slits, a liquid nitrogen-cooled Ge photodiode detector, a lock-in amplifier and a Macintosh Plus computer using LabView software for data acquisition.

RESULTS

Reaction of MMPP with chloride in D₂O/H₂O (1:1) at low pH gives a high yield of singlet oxygen which can be readily detected by our apparatus. Spectral determination confirmed that the luminescence has the characteristics of singlet oxygen monomol emission. This decay curve is well fit by an exponential, suggesting that the reaction is first-order or pseudo-first order in MMPP.

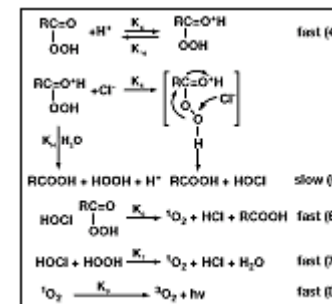
For quantitative determination of singlet oxygen, we chose the reaction of N-chlorosuccinimide (NCS) and hydrogen peroxide as standard. The singlet oxygen yield for this reaction is 93%. The singlet oxygen yields from the MMPP reaction with chloride was then determined by comparison to the NCS standard which showed that two moles of

monoperoxyacid are required to form one mole of singlet oxygen; and since one mole of MMPP salt contains two moles of monoperoxyacid, the yield is 42% of theoretical based on monoperoxy acid.

Although MMPP undergoes slow hydrolysis to hydrogen peroxide, the rate of its formation in acidic medium is too slow to be important in the MMPP plus chloride kinetics at high chloride ion concentration.

DISCUSSION

A reasonable mechanism for the production of singlet oxygen in this system involves rapid protonation of MMPP followed by oxidation of chloride ion to hypochlorous acid; the latter then reacts rapidly with another mole of peroxyacid to generate singlet oxygen. This is consistent with the luminescence and kinetic data:



DISCUSSION (cont.)

Rate Constants for Reaction of MMPP with Chloride Ion

Parameter	Titration	¹ O ₂ Decay
k _H , s ⁻¹	0.074/K _e	0.065/K _e
k ₅ , M ⁻¹ s ⁻¹	2.66/K _e	2.73/K _e
k ₅ /k _H , M ⁻¹	35.9	42.0

k_H = Rate of peroxyacid hydrolysis to hydrogen peroxide and carboxylic acid

k₅ = Rate of formation of hypochlorous acid from chloride ion and peroxyacid

CONCLUSION

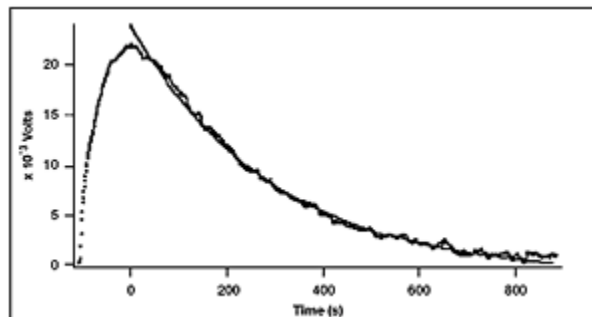
In conclusion, MMPP at acidic pH decomposes rapidly in the presence of chloride ion to yield quantitatively singlet oxygen.

Other evidence:

No singlet oxygen is produced from hydrogen peroxide and chloride ion. Peroxyacid is essential.

In the absence of chloride ion, MMPP itself does not produce singlet oxygen.

By monitoring the singlet oxygen emission, we found that the overall rate constants for the reaction of MMPP and H₂O with HOCl (k₆ and k₇, respectively) are at least 30 times faster than the rate constant for the reaction of MMP with chlorite ion (k₅). This result validates the use of steady-state kinetics.



Singlet Oxygen IR Emission and First-order Fit of the Reaction Between MMP (0.070M) and KCl (0.36M) in D₂O/H₂O (1:1, pH 2.7) at 40°C