

# Evidence for generation of singlet oxygen from ozone

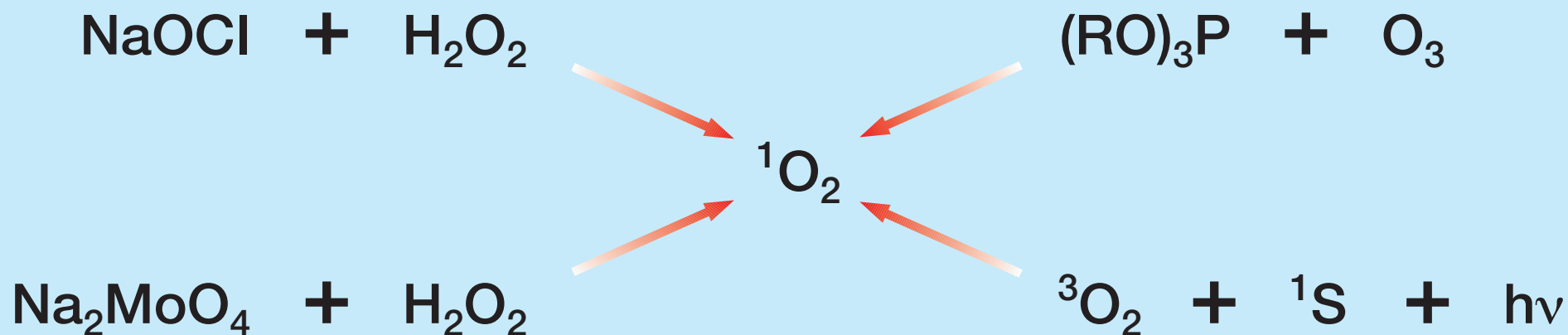
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Ozone has found large-scale technical application as selective oxidant to cleave double bonds in fine chemicals synthesis [1]. In our efforts to expand its application we investigated possibilities to derive secondary oxidants by the reaction of ozone with suitable substrates - singlet oxygen being such a candidate. Singlet oxygen is the lowest excited state of molecular oxygen with unique properties with respect to chemical selectivity, product distribution, and mildness of reaction conditions. Usually it is generated by a photosensitization [2]. To enhance its applicability, chemical methods for the generation of singlet oxygen have been developed. The most well-known source is based on the oxidation

of hydrogen peroxide by sodium hypochlorite [3]. A more recent method involves the disproportionation of hydrogen peroxide catalyzed by molybdate ions to yield quantitatively singlet oxygen and water [4]. In contrast to oxygen, both ozone and singlet oxygen are molecules in the singlet state [5]. Accordingly, singlet oxygen should be available from ozone by formal transfer of one oxygen to a suitable substrate. Consequently various reactions of this type have been found: Murray *et al.* have described phosphite ozonides [6], which form by low-temperature reaction of phosphites with ozone and are cleaved to form phosphate and singlet oxygen.

Scheme 1: Commonly used methods for the generation of singlet oxygen



Further systems capable of generating singlet oxygen from ozone comprise ether hydrotrioxides [7], silyl hydrotrioxide [8], certain biological molecules [9], and chlorine dioxide [10].



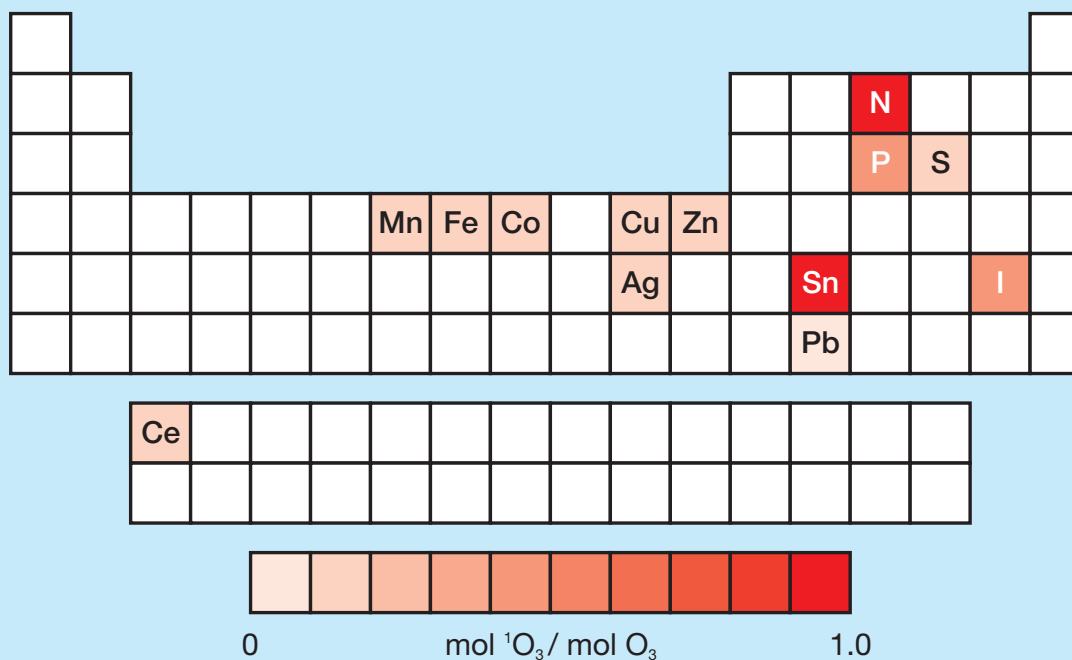
## Singlet oxygen detected by Luminescence

The unambiguous proof for the generation of singlet oxygen can be gained from its radiative decay at 1270nm [12]. However, only a minute amount of singlet oxygen returns to the ground state by emission of radiation in the condensed phase, while the major amount is deactivated through collision with solvent molecules. Therefore, it is necessary to carefully exclude stray-light and to resort to a highly sensitive near-IR

detector able to monitor selectively the  $^1\text{O}_2$  luminescence. As expected from lifetimes of singlet oxygen in ordinary water and deuterium oxide [13], the intensity of the emission (Figure 2) was strongly increased throughout by using deuterium oxide instead of water. For this change of the solvent it is reasonable to assume that no change in the mechanism of the reaction between ozone and the substrate will occur.

Figure 2

Efficiency of singlet oxygen generation from solutions of inorganic salts in acetic acid and water upon ozonization as detected by luminescence in comparison to the system  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O} + \text{H}_2\text{O}_2$ .



From Figure 2 it could be concluded that several metal ions, such as  $\text{Ce}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Mn}^{3+}$ , and  $\text{Co}^{2+}$ , which showed activity in the ozone uptake (Figure 1), are not effective in the generation of singlet oxygen. One might expect this behavior since their ions are prone to one-electron transfer reactions resulting in intermediate radical species. Thus, from literature it is known, that manganese salts, and in peculiar manganese(III)acetate, oxidize acetic acid by a radical mechanism, giving intermediate acetoxy radicals. These have been exploited beneficially for the oxidation of benzylic methyl- and methylene-groups under strongly acidic conditions [13-16].

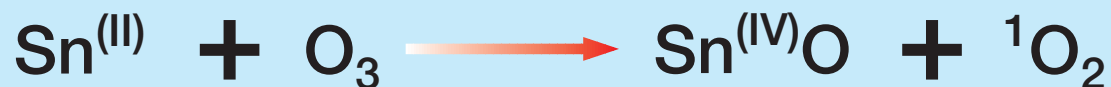
In conclusion, only a few systems were found, which were promoters of the reaction of ozone to singlet oxygen (Figure 2), obviously by two-electron transfer oxidation. This might be rationalized by an ionic, non-

radical mechanism. The most active promoters of singlet oxygen from ozone were found to be tin(II)acetate in acetic acid and sodium nitrite in water, showing an efficiency as high as 67% and 70% .

Tin(II) acetate in acetic acid showed the fastest reaction rate, which is apparently independent of the concentration of the reducing species in solution. It was found to be only limited by mass transfer over the phase boundary. All other reducing agents showed a dependence of the luminescence intensity both from the concentration in solution and concentration of ozone in oxygen.

If one takes into account the possibility to reduce the formed tin(IV), the high efficiency of singlet oxygen generation by the newly found way might lead to new applications of this powerful reagent in synthetic organic chemistry.

Scheme 2: Proposed mechanism for the reaction of Sn(II) with ozone, giving singlet oxygen



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