Evidence for the Generation of Singlet Oxygen ($^1O_2$, $^1\Delta_g$) from Ozone Promoted by Inorganic Salts

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Summary. Evidence for novel chemical sources of singlet oxygen based on the conversion of ozone by tin(II) in acetic acid or nitrite ions in water was found by screening a selection of inorganic salts by means of a sensitive detector for exothermic processes (SEDEX) and a N_2-cooled Ge-diode for singlet oxygen luminescence measurements.

Keywords. Ozonization; Luminescence detection; Sn(II); Nitrite; SEDEX.

Introduction

Ozone has found large-scale technical applications as a 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 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].

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In contrast to molecular 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 yield phosphate and singlet oxygen. This has been disputed by others who found that the presumed singlet oxygenation took place at a temperature far below the decomposition temperature of the phosphite-ozone adduct [7]. A recently published investigation by *Mori et al.* [8] describes two pathways of the reaction of triphenylphosphite-ozonide in detail deduced from the distribution of the products and kinetic measurements. Further systems capable of generating singlet oxygen from ozone comprise ether hydrotrioxides [9], silyl hydrotrioxide [10], certain biological molecules [11], and chlorine dioxide [12].

In this report we describe the results of a screening of a series of inorganic salts with respect to their capacity to promote the generation of singlet oxygen from ozone.

Results and Discussion

Reactions of Ozone Detected by Temperature Increase

A selection of metal salts was screened for their ozone converting properties in acetic acid solution. Acetic acid was chosen as the solvent since it is known to be more or less inert towards oxidation by ozone under our experimental conditions. Furthermore, an acidic medium was preferred to avoid malicious side effects from radical-type ozone decomposition in basic media [13]. When available, the acetates were used to avoid potentially exothermic side reactions from oxidation of the, *e.g.*, chloride counterion. In a primary screening, all compounds were subjected to ozonization and tested for their capability of conversion of ozone by measuring the ozone uptake and the increase in temperature. This was achieved by using the SEDEX ("SEnsitive Detector for EXothermic processes") apparatus, which also provided sufficient safety for assessing potentially hazardous chemical reactions.

Using these criteria and the data obtained by the SEDEX many salts could be ruled out (Fig. 1) as potential promoters of singlet oxygen from ozone due to a lacking increase in temperature and a lacking ozone consumption during ozonization. Besides several transition metal ions like iron(II) or cerium(III), which promoted ozone uptake and led to a temperature increase, the tin(II) ion occurred as remarkable candidate for promoted singlet oxygen generation.

Singlet Oxygen Detected by Luminescence

The unambiguous proof for the generation of singlet oxygen can be gained from its radiative decay at 1270 nm [14]. 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 $^1O_2$ luminescence.
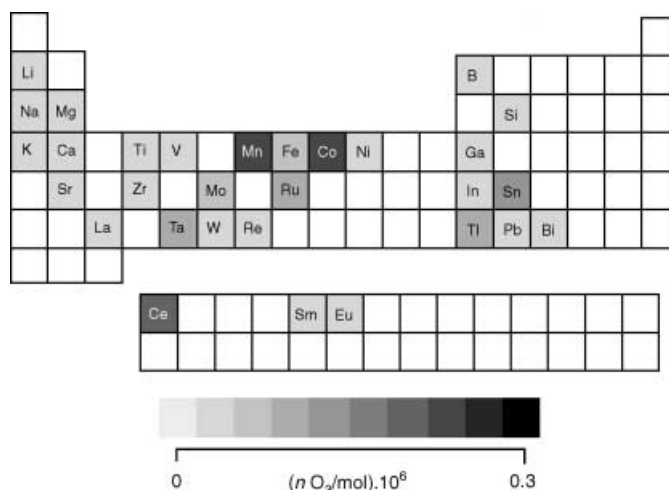
Fig. 1. Ozone uptake $((n\,O_3/mol) \cdot 10^6)$ of inorganic compounds in acetic acid using a SEDEX experiment. Compounds used: $Li(CH_3COO)$, $Na(CH_3COO)$, $K(CH_3COO)$, $Mg(CH_3COO)_2 \cdot 4H_2O$, $Ca(CH_3COO)_2$, $Sr(CH_3COO)_2 \cdot H_2O$, $La(CH_3COO)_3 \cdot H_2O$, $Sm(CH_3COO)_3 \cdot H_2O$, $Eu(CH_3COO)_3 \cdot H_2O$, $Ce(CH_3COO)_3 \cdot H_2O$, $B_2O(CH_3COO)_4$, Ga_2O_3, $In(CH_3COO)_3 \cdot H_2O$, $Tl(CH_3COO)$, $Zr(CH_3COO)_3OH$, $Si(CH_3COO)_4$, $Sn(CH_3COO)_2$, $Pb(CH_3COO)_4$, V_2O_5, Ta_2O_5, $Bi(CH_3COO)_3$, MoO_3, $Mn(CH_3COO)_2 \cdot 4H_2O$, $Mn(CH_3COO)_3 \cdot 2H_2O$, CH_3ReO_3, $FeSO_4 \cdot 7H_2O$, RuO_2, $Co(CH_3COO)_2 \cdot 4H_2O$, $Ni(CH_3COO)_2$, $LiTiO_3$, $Na_2MoO_4 \cdot 2H_2O$, and H_2WO_4
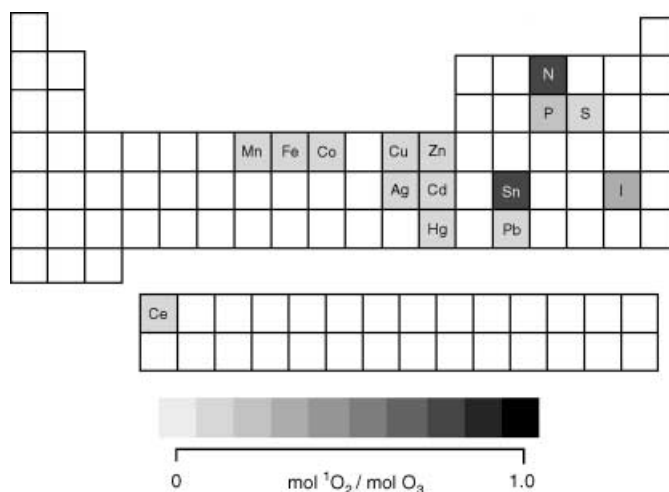
Fig. 2. Efficiency of singlet oxygen generation (mol $^1O_2$/mol O_3) from solutions of inorganic salts in acetic acid[a] and water[b] upon ozonization as detected by luminescence in comparison to the system $Na_2MoO_4 \cdot 2H_2O + H_2O_2$[a]. Compounds used: Cu_2O[a], $AgNO_3$[a], $Zn(CH_3COO)_2$[a], $Cd(CH_3COO)_2$[a], $Hg(CH_3COO)_2$[a], $Ce(CH_3COO)_3 \cdot H_2O$[a], $Ce(SO_4)_2 \cdot 4H_2O$[a], $Sn(CH_3COO)_2$[a], $Pb(CH_3COO)_2 \cdot 3H_2O$[a], $Mn(CH_3COO)_2 \cdot 4H_2O$[a], $Mn(CH_3COO)_3 \cdot 2H_2O$[a], $FeSO_4 \cdot 7H_2O$[a], $Co(CH_3COO)_2 \cdot 4H_2O$[a], $NaNO_2$[b], $NaH_2PO_2 \cdot H_2O$[a], $Na_2HPO_3 \cdot 5H_2O$[b], Na_2SO_3[a], KI[a], KIO_3[a]

As expected from known lifetimes of singlet oxygen in ordinary water and deuterium oxide [15], the intensity of the emission (Fig. 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.

From Fig. 2 it could be concluded that several metal ions, such as Ce^{3+}, Mn^{2+}, Mn^{3+}, and Co^{2+}, which showed activity in the ozone uptake (Fig. 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 acetyl radicals. These have been exploited beneficially for the oxidation of benzylic methyl- and methylene-groups under strongly acidic conditions [16–19].

In addition to the salts investigated by the SEDEX method with acetic acid as the solvent, salts involving a series of anions were tested also partly in aqueous solutions. In conclusion, only a few systems were found, which were promoters of the reaction of ozone to singlet oxygen (Fig. 2), obviously by a two-electron transfer oxidation. This might be rationalized by an ionic, non-radical mechanism. The most active promoters of singlet oxygen formation from ozone were found to be tin(II) acetate in acetic acid and sodium nitrite in water, showing efficiencies 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 the concentration of ozone in oxygen.

If one takes into account the possibility to reduce the formed tin(IV) back to tin(II) together with the high efficiency of singlet oxygen generation, this system might lead to new applications in organic synthesis.

Experimental

Ozone was generated by OZONE GENERATOR BMT 802X, BMT Messtechnik Berlin. The flux of oxygen was $0.5\,dm^3$ O_2/min at standard pressure. Ozone was monitored by the OZONE ANALYZER BMT 963 VENT, BMT Messtechnik Berlin; OSTI, Walnut Creek, CA, using optical absorption. The values given are g Ozone/m^3 ($0°C$, $10^2\,kPa$) and are corrected for pressure and temperature. These monitors were used for all SEDEX and luminescence experiments.

Ozonizations were carried out in a $20\,cm^3$ vessel equipped with a mechanical stirrer, gas inlet pipe with a frit, a reflux cooler in the off-gas stream, and a Ni/CrNi-thermocouple. Solutions of $400\,\mu mol$ of metal ions in $20\,cm^3$ of acetic acid were prepared, resulting in a final concentration of $20\,mmol$ metal ions/dm^3, which were thermostated to $20°C$ in the SEDEX apparatus while a stream of dry N_2 was passed through the solutions.

The SEDEX apparatus (Systag, System Technik AG, Rüschlikon, CH) consisted of an oven, which provided the continuous monitoring of potentially harmful and exothermic reactions. It allows visual observation of the sample under investigation. After equilibration, the solutions were subjected to ozonization while measuring the temperature inside and outside of the reaction vessel as well as the ozone concentrations being applied to the solution and the one passing out of the vessel. The oxygen flux was $0.5\,dm^3$ O_2/min, the ozone concentration being produced by the ozone generator was $80\,g$ O_3/m^3 ($p = 10^2\,kPa$, $T = 0°C$). The solutions were ozonized for times up to $1000\,s$ while stirring thoroughly to ensure efficient mass transfer to the liquid phase.

The luminescence originating from the sample cell was detected by a N_2 cooled Ge-diode detector from North Coast Scientific Corp., Model EO-817L, connected to a lock-in amplifier from Stanford Research Systems Model SR830 DSP. The detector was powered by a North Coast Scientific Corp. Model Bias Supply Model 823A. The apparatus for the luminescence measurement was calibrated by means of a standard experimental setup utilizing the sodium molybdate/H_2O_2 system [4] in H_2O: to a solution of 484 mg of $Na_2MoO_4 \cdot 2H_2O$ in 10 cm^3 H_2O was added a solution of 570 mm^3 of 50 wt% H_2O_2 (equalling 10 mmol of 100% H_2O_2). This system is known to give a quantitative yield of singlet oxygen, thus resulting in a total amount of 5 mmol of singlet oxygen [4]. The geometry of the setup was kept constant for all experiments.

Acknowledgments

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