First evidence for singlet molecular oxygen, $^1O_2$ ($^1\Delta_g$), generation from polyoxometalate and hydrogen peroxide

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Abstract: Singlet oxygen is a powerful and selective oxidant, which can be used in biosynthetic syntheses. Only few efficient chemical sources involving the catalytic decomposition of hydrogen peroxide into this excited species has been found. We evidenced for the first time the formation of $^1O_2$ catalyzed by polyoxometalates, more particularly polyoxoniobate. The new systems have successfully been applied to the oxidation of hydrophilic and hydrophobic substrates either in water or in (micro)emulsion systems using amphiphilic polyoxoniobate.

Keywords: Singlet oxygen, Catalysis, Oxidation, Polyoxoniobate, Hydrogen peroxide.

1. Introduction

Singlet molecular oxygen, $^1O_2$ ($^1\Delta g$), is a powerful and selective oxidant very useful to prepare oxygenated intermediates for fine chemistry.[1] There are several methods for generating this excited species in solution, either chemical, such as the disproportionation of hydrogen peroxide catalyzed by molybdate ions, or photochemical via the dye-sensitized photochemical excitation of $^3O_2$.[2] The latter technique has largely been used in organic synthesis.[3] However, it requires specific photochemical reactors which can be dangerous on an industrial scale; therefore, it has found very few applications. On the contrary, chemical sources of $^1O_2$, involving inexpensive and readily available oxidants such as H_2O_2, could be attractive alternatives to the usual photochemical method, providing only water as a by-product.[4] The H_2O_2/MoO_4^{2-} system is the most efficient one with a quantitative yield of $^1O_2$ generation in water.[5] Tungstate ions behave in a similar way but 3 times slower. Other relevant sources are based on La(III), and Ca(II), with 40 and 25% $^1O_2$ yield respectively. On the other hand, research applications of polyoxometalates (POM) have over the past two decades become very important. These catalysts are known to activate both oxygen and hydrogen peroxide and have been widely used to carry out oxidation reactions such as epoxidation, sulfide oxidation, etc. However, the generation of $^1O_2$ has never been put forward until now except by Neumann who showed ene type reactivity for $H_2O_2/[Zn_2Bi^{III}_2(ZnW_9O_{34})_2]^{14-}$ system on alkenes and dienes which is a hallmark of $^1O_2$.[6]

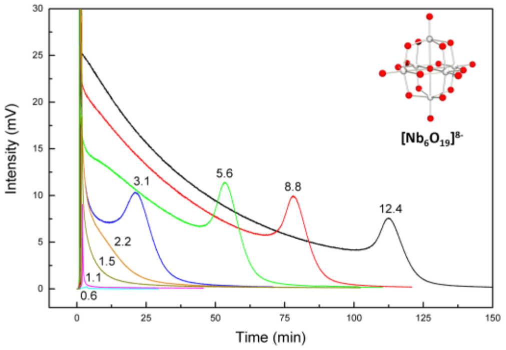

Figure 1. IR luminescence signals emitted at 1270 nm at 30°C from D_2O solutions containing $K_8Nb_6O_{19}$ (0.02 M) and different amounts of H_2O_2 expressed by the ratio H_2O_2/Nb_{atom}.

In this context, we evidenced for the first time the formation of $^1O_2$ from the decomposition of H_2O_2 catalyzed by POMs, not only by the previously reported $[Zn_2Bi^{III}_2(ZnW_9O_{34})_2]^{14-}$ but also by polyoxoniobates (PONb) like $[Nb_6O_{19}]^{8-}$. The systems have been investigated by detection of the specific $^1O_2$ luminescence at 1270 nm (Figure 1) which constitutes a direct and unambiguous proof of the formation of the excited species.

2. Experimental (or Theoretical)

A typical chemiluminescence experiment was carried out as follows. A solution containing the catalyst in D_2O or H_2O was placed in the thermostated brass cell holder, via a quartz cell, and stirred at desired temperature. Once the background noise of the IR signal was stabilized, H_2O_2 (50%) was introduced and the intensity of the luminescence signal at 1270 nm was recorded as a function of time. The intensity of the signal is related to the rate of $^1O_2$ generation and the total area under the curve is directly related to the cumulated amount of singlet oxygen. The oxidation of α-terpinene was carried out in a glass vial, 15 µmol of catalyst, 3 ml of solvent with O/W at the desired ratio (0.33 M of α-terpinene), 1.1 equiv. H_2O_2 was added. The sample is emulsified with an Ultra-Turrax® (11,500 rpm, 1 min) and heated at 40°C, 300 rpm for 2 h. The products were identified and quantified by ^1H and ^{13}C NMR.

3. Results and discussion

Several parameters have been investigated: the nature of the POM, the H_2O_2/Nb ratio, the temperature, the pH, the recyclability of the catalytic system, the solvent in order to determine the optimal conditions for oxidation reactions. Attempts to identify the reactive intermediate(s) have also been conducted though the Nb chemistry is highly complex.[7] For example, we found that the $H_2O_2/K_8Nb_6O_{19}$ system, in the presence of 3 equivalents of H_2O_2 per niobium atom, affords the formation of $^1O_2$ with a 65% yield under acidic conditions (pH = 4 - 7), unlike all previously reported systems which operate under alkaline conditions. The efficiency of the $H_2O_2/K_8Nb_6O_{19}$ system to oxidize organic substrates was finally demonstrated with anthracene-9,10-divinylsulfonate, a specific water-soluble chemical trap of $^1O_2$. But in order to oxidize hydrophobic substrate, a biphasic medium is required, as we showed in our previous work that amphiphilic POMs can spontaneous from nanoparticles which stabilize biphasic emulsion systems, we synthetized an amphiphilic PONb obtained by ion exchange with an alkylammonium salt.[8] A screening of solvent allowed to find emulsions systems, especially Pickering one. The most relevant of these systems, based on a green solvent, cyclopentyl methyl ether (CPME), achieved a total conversion of a model substrate, α-terpinene, in 2 h at 40°C in a 75/25 CPME/Water mixture (Table 1). The catalyst could be reused 5 times without loss of activity.

Solvent	Ratio O/W	Catalyseur	Conv. (%)
CPME/Water	75/25	$K_8Nb_6O_{19}$	< 1
CPME	100/0	$K_8Nb_6O_{19}$	28
CPME	100/0	$(C_{16})_8Nb_6O_{19}$	87
CPME/Water	**75/25**	$\mathbf{(C_{16})_8Nb_6O_{19}}$	**98**

Table 1. Oxidation of α-terpinene with polyoxoniobate catalyst (conditions described in experimental part).

4. Conclusions

PONbs catalyze efficiently the decomposition of H_2O_2 into $^1O_2$, 65 % for $K_8Nb_6O_{19}$, even at low pH. And it is the first evidence of $^1O_2$ formation for POM, which open a new field of application for these compounds. To finish, the systems are very promising and the scope of substrates has been extended to compounds of interest and to other media such as emulsions and Pickering emulsions. However, deeper investigations are required to find the mechanism.

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