

Identification of the precursor of singlet oxygen ($^1\text{O}_2$, $^1\Delta_g$) involved in the disproportionation of hydrogen peroxide catalyzed by calcium hydroxide

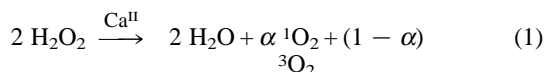
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Catalytic disproportionation of hydrogen peroxide by calcium hydroxide generates singlet molecular oxygen $^1\text{O}_2$ ($^1\Delta_g$) through the diperoxohydrate peroxide $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$ with a 50% yield based on the calcium peroxide.

Many inorganic compounds are known to induce the disproportionation of hydrogen peroxide into singlet oxygen ($^1\text{O}_2$, $^1\Delta_g$).¹ Among them, calcium hydroxide appears both attractive for its environmental friendly feature and amazing on account of the simplicity of the catalyst involved [eqn. (1)].



Although the formation of $^1\text{O}_2$ during reaction (1) has been established,¹ several points remain unclear: (i) the traps of $^1\text{O}_2$ bore carboxylate functions which precipitated partially in presence of the calcium salts, (ii) the calcium hydroxide did not have the highest purity commercially available, (iii) the influence of the main parameters on the reaction were not studied, (iv) no information was provided with regard to the nature of the precursor of $^1\text{O}_2$. Therefore, the system $\text{H}_2\text{O}_2/\text{Ca}^{\text{II}}$ has been reinvestigated by resorting to two complementary techniques: the detection of the IR luminescence of $^1\text{O}_2$ at 1270 nm and the chemical trapping with a more suitable trap. In a second step, the nature of the precursor and the yield of $^1\text{O}_2$ were determined.

The monomol emission of $^1\text{O}_2$ was detected with a liquid-nitrogen cooled germanium diode equipped with a bandpass filter for $1270 \pm 10 \text{ nm}$.² The assays were carried out in a thermostated cell at 50°C filled with an aqueous (H_2O or D_2O) solution of H_2O_2 (1.0 M). After recording the baseline, solid CaO (0.2 M) of high purity (99.995%) was added and the photoemission of $^1\text{O}_2$ was monitored. The maximum values of the luminescence intensity I_p are reported in Table 1.

The luminescence intensity I_p was found to be strongly dependent on the deuteration of the solvent (Table 1, entries 1 and 2) as a ten-fold increase was observed in deuterated water (95%), in good agreement with the longer lifetime of $^1\text{O}_2$ in D_2O than in H_2O .³ In a control experiment (Table 1, entry 3), it

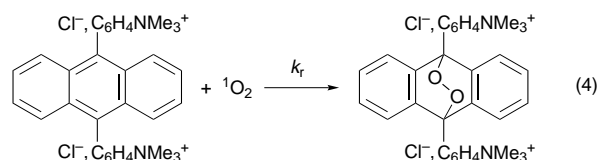
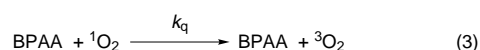
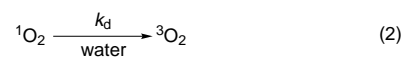
Table 1 Experimental conditions and emission intensity I_p of $^1\text{O}_2$ luminescence^a

Entry	Calcium compound	$[\text{H}_2\text{O}_2]/$ mmol	$[\text{NaOH}]/$ mmol	Solvent	I_p/mV
1	CaO	5.0	—	H_2O	0.4 ± 0.1
2	CaO	5.0	—	D_2O	4.4 ± 0.5
3	—	5.0	2.0	D_2O	No signal
4	$\text{CaO}_2 \cdot 8\text{H}_2\text{O}$	—	—	D_2O	0.3 ± 0.1
5	$\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$	—	—	CD_3OD	0.5 ± 0.1
				D_2O	10 ± 0.5
				CD_3OD	98 ± 2

^a Experiments were carried out with 1.0 mmol of calcium compounds at 50°C in 5 ml of solvent.

was shown that the disproportionation of H_2O_2 (1 M) induced by NaOH (0.4 M) did not provide any detectable signal in contrast with the finding of Smith and Kulig.⁴ Accordingly, $^1\text{O}_2$ arises from the interaction between Ca^{II} and H_2O_2 and not from the base-catalyzed disproportionation of H_2O_2 .

The detection of $^1\text{O}_2$ via its IR luminescence requires a relatively high steady-state concentration of $^1\text{O}_2$.⁵ Thus, experiments with the system $\text{H}_2\text{O}_2/\text{Ca}^{\text{II}}$ were carried out in D_2O and with gentle warming (50°C). On the other hand, specific chemical trapping worked in ordinary water, at room temperature, and was found to be more reliable for the quantification of $^1\text{O}_2$ than the spectral method. The new cationic water-soluble trap, 9,10-bis(4-trimethylphenylammonium) anthracene dichloride (BPAA), which efficiently reacts with $^1\text{O}_2$ giving a specific endoperoxide BPAAO_2 as the sole product,⁶ was particularly suitable for these trapping experiments since it did not interfere with the catalytic reaction as the tetrapotassium rubrene-2,3,8,9-tetracarboxylate (RTC) did.¹ In presence of BPAA, $^1\text{O}_2$ arising from reaction (1) can either be quenched by water [eqn. (2)] and by BPAA [eqn. (3)] or react with this trap [eqn. (4)].⁷



Under pseudo-stationary conditions ($d[^1\text{O}_2]/dt = 0$), processes (1)–(4) lead to eqn. (5) giving the rate of the disappearance of BPAA:

$$\frac{d[\text{BPAA}]}{dt} = -v(^1\text{O}_2) \frac{k_r[\text{BPAA}]}{k_d + (k_r + k_q)[\text{BPAA}]} \quad (5)$$

where $v(^1\text{O}_2)$ is the rate of $^1\text{O}_2$ generation from reaction (1).

The concentration of BPAA used was very low (10^{-4} M) in order to minimize the disturbance of the process under study. Under these conditions, the quenching of $^1\text{O}_2$ by water is the main pathway for $^1\text{O}_2$ decay. Thus, $k_d \gg (k_r + k_q)[\text{BPAA}]$ and eqn. (5) reduces to eqn. (6) which allows calculation of $v(^1\text{O}_2)$ from the initial rate of BPAA disappearance, $d[\text{BPAA}]/dt$:

$$v(^1\text{O}_2) = -\frac{d[\text{BPAA}]}{dt} \frac{k_d}{k_r[\text{BPAA}]} \quad (6)$$

In control experiments, it was shown that the oxidation of BPAA (10 mM) gives the expected endoperoxide BPAAO_2 identified by ^1H and ^{13}C NMR spectroscopy.⁶ Accordingly, the

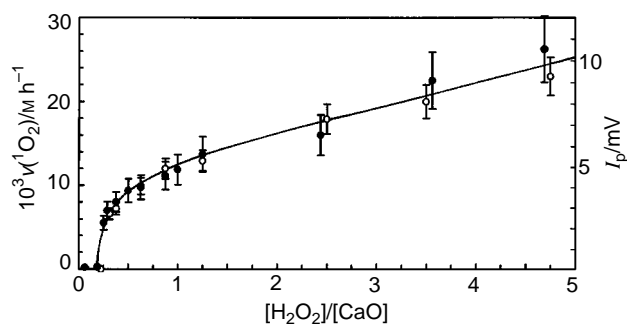
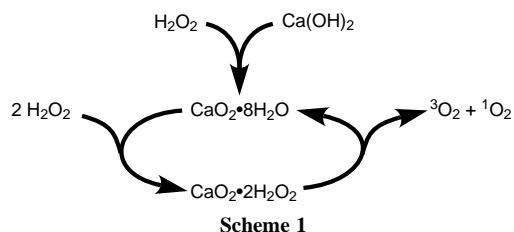


Fig. 1 $^1\text{O}_2$ formation as a function of $[\text{H}_2\text{O}_2]$ detected by chemical trapping (○) (200 mM CaO, 0.1 mM BPAA, H_2O , 25 °C) or by IR luminescence at 1270 nm (●) (same conditions except D_2O , 50 °C)

disappearance of BPAA could be confidently assigned to an oxidation through $^1\text{O}_2$. It was also shown that 50 mM CaO was able to disproportionate 500 mM H_2O_2 indicating that the Ca^{II} involved in process (1) acts as a catalyst. It is noteworthy that, whereas no H_2O_2 could be detected in the aqueous phase at the end of the reaction, the precipitate was found to contain exactly one peroxide group per Ca^{II} whatever the starting concentrations of H_2O_2 and CaO were. The final product is then probably the hydrated calcium monoperoxide $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$ which is known to be stable in water.^{8,9} The rate of $^1\text{O}_2$ formation was measured for various initial concentrations of H_2O_2 (Fig. 1).

This figure shows that the formation of $^1\text{O}_2$ requires at least 1 equiv. of H_2O_2 . The reaction rate increases steeply at first and then moderately when the concentration of H_2O_2 is increased suggesting that the main precursor of $^1\text{O}_2$ is probably the calcium complex which bears the highest number of peroxy groups. It is noteworthy that chemical trapping and detection of the luminescence provided similar results since a mere standardization allowed the fitting of both curves.

Although numerous calcium peroxides are reported in the literature,^{8–10} Karelin *et al.* have recently established that only two well defined compounds may be obtained by reaction of H_2O_2 with CaO in aqueous solution. The first is the stable octahydrate peroxide $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$ and the other is the unstable diperoxohydrate peroxide $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$ which decomposes spontaneously releasing oxygen.¹⁰ Up to now, no report has dealt with the multiplicity of the oxygen. We looked for the possible $^1\text{O}_2$ luminescence emitted by thermolysis at 50 °C of the calcium peroxides $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$ and $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$ dispersed in deuterated methanol and water (Table 1). Deuterated solvents were preferred to take advantage of the longer lifetime of $^1\text{O}_2$ which provides an enhanced intensity of the luminescence. $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$ did not emit any significant luminescence (Table 1, entry 4) whereas a similar amount of $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$ emitted a huge signal (98 ± 2 mV) in CD_3OD . In D_2O , the signal was significant but lower probably owing to hydrolysis of the



complex as for the peroxomolybdates.¹¹ Accordingly, we can assert that $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$ is a precursor of $^1\text{O}_2$. A catalytic scheme may be drawn from this conclusion (Scheme 1).

In a first step, $\text{Ca}(\text{OH})_2$ is converted into $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$ which binds two molecules of H_2O_2 giving $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$. On thermolysis at moderate temperature, this latter peroxide splits up into $^1\text{O}_2$ and $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$. This catalytic cycle would operate until complete disproportionation of H_2O_2 and would leave $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$ as a final product.

In order to assess the efficiency of $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$ to generate $^1\text{O}_2$, the oxidation of 250 mM α -terpinene was performed by warming at 50 °C a suspension of 400 mM $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$ in CD_3OD . α -Terpinene is known to trap efficiently all the $^1\text{O}_2$ released giving mainly ascaridol.¹² ^1H NMR analysis of the reaction mixture showed that, under these conditions, $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$ converts 85% of α -terpinene into ascaridol providing a yield of $^1\text{O}_2$ formation equal to $50 \pm 3\%$ based on this calcium peroxide.

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Notes and References

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