Lanthanum(III)-Catalyzed Disproportionation of Hydrogen Peroxide: A Heterogeneous Generator of Singlet Molecular Oxygen—$^1O_2$ ($^1\Delta_g$)—in Near-Neutral Aqueous and Organic Media for Peroxidation of Electron-Rich Substrates

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Abstract: The decomposition of hydrogen peroxide into singlet molecular oxygen—$^1O_2$ ($^1\Delta_g$)—in the presence of lanthanum(III) salts was studied by monitoring its characteristic IR luminescence at 1270 nm. The process was found to be heterogeneously catalyzed by La^{III}, provided that the heterogeneous catalyst is generated in situ. The yield of $^1O_2$ generation was assessed as $45 \pm 5\,\%$ both in water and in methanol. The pH-dependence on the rate of $^1O_2$ generation corresponds to a bell-shaped curve from pH 4.5 to 13 with a maximum around pH 8. The study of the influence of H_2O_2 showed that the formation of $^1O_2$ begins as soon as one equivalent of H_2O_2 is introduced. It then increases drastically up to two equivalents and more smoothly above. Unlike all other metal salt catalyst systems known to date for H_2O_2 disproportionation, this chemical source of $^1O_2$ is able to generate $^1O_2$ not only in basic media, but also under neutral and slightly acidic conditions. In addition, this La-based catalyst system has a very low tendency to induce unwanted oxygenating side reactions, such as epoxidation of alkenes. These two characteristics of the heterogeneous lanthanum catalyst system allow non-photochemical (i.e., "dark") singlet oxygenation of substrate classes that cannot be peroxidized successfully with conventional molybdate catalysts, such as allylic alcohols and alkenyl amines.

Keywords: heterogeneous catalysis · hydrogen peroxide · lanthanum · luminescence · peroxidation · singlet oxygen

Introduction

The "dark" singlet oxygenation of organic compounds through catalytic disproportionation of hydrogen peroxide is of industrial relevance because this method can be easily implemented in common stirred tank reactors, thus eliminating the need for dedicated photoreactors currently required for singlet oxygenation through photooxidation. Accordingly, we are interested in the development of novel catalysts for hydrogen peroxide disproportionation with improved efficiency and broader windows of application. In 1985, Aubry screened the periodic table in search of chemical generators of singlet molecular oxygen—$^1O_2$ ($^1\Delta_g$)—based on hydrogen peroxide decomposition.[1] More than thirty systems were found to be able to produce the excited species in alkaline aqueous medium (pH ≈ 12). However, as the $^1O_2$ detection by chemical trapping experiments were all performed under similar conditions of temperature, pH, and reactant concentrations, each system has to be further reinvestigated separately to optimize reaction conditions. Systems based on molybdenum(VI), tungsten(VI), and calcium(II) have been reviewed in detail.[2–17] Lanthanides were also found to be efficient in the screening experiments, and it appeared judicious to reexamine lanthanum because it is inexpensive and has a low toxicity. This work reports the study of the decomposition of H_2O_2 by lanthanum(III) salts by measurement of the characteristic IR luminescence of $^1O_2$ at 1270 nm. In addition, preparative examples of La-catalyzed "dark" singlet oxygenation of some alkenes are provided, and the synthetic added value of this new catalyst system over already known systems is illustrated.

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Results and Discussion

Influence of the nature of the lanthanum salt: When $^1O_2$ is generated, by any means, in a liquid in the absence of substrate, it can disappear according to two physical pathways of deactivation [Eq. (1) and Eq. (2)].[18]

$$^1O_2 \xrightarrow[\text{solvent}]{k_d} {}^3O_2 \quad (1)$$

$$^1O_2 \xrightarrow{k_p} {}^3O_2 + h\nu\ (1270\ \text{nm}) \quad (2)$$

The first pathway (k_d) is the quenching of $^1O_2$ by the solvent, whereas the second (k_p) corresponds to the radiative deactivation of $^1O_2$ with emission of one photon at 1270 nm. In conventional solvents, this latter reaction is of minor importance, but highly specific to $^1O_2$. Hence, the recording of the luminescence at 1270 nm proves the involvement of $^1O_2$ in the process under study. In a first experiment, we examined the decomposition of H_2O_2 (1M) induced by a lanthanum salt (0.1M) in alkaline aqueous solution (H_2O, $pH = 9.0$). Four different lanthanum(III) salts were studied: the hydroxide $La(OH)_3$, the oxide La_2O_3, the nitrate $La(NO_3)_3 \cdot 6H_2O$, and the chloride $LaCl_3 \cdot 7H_2O$. The maximum intensities, I_{max}, of the luminescence signals when the stationary state is reached are reported in Table 1.

Table 1. Maximum intensities of the luminescence signal at 1270 nm for different H_2O_2 (1M)/La^{III} (0.1M) systems measured in H_2O at $pH = 9.0 \pm 0.1$ and $T = 25\,^\circ C$.

Nature of the salt	$La(OH)_3$	La_2O_3	$La(NO_3)_3 \cdot 6H_2O$	$LaCl_3 \cdot 7H_2O$
I_{max} [mV]	1.0 ± 0.5	1.0 ± 0.5	46 ± 2	41 ± 2

The insoluble lanthanum oxide and hydroxide each provide a very weak signal (≈ 1 mV), whereas much larger signals (≈ 45 mV) are obtained with the water-soluble lanthanum nitrate and chloride as soon as they are precipitated at pH 9 by addition of NaOH in the presence of H_2O_2. On the other hand, no signal is detected for the starting homogeneous solutions containing only H_2O_2 and $La(NO_3)_3 \cdot 6H_2O$ or $LaCl_3 \cdot 7H_2O$ at natural pH (≈ 3.5). These results suggest that the process of $^1O_2$ generation is heterogeneous and that the formation of the intermediates, probably peroxolanthanum species,[19–21] is favored when the starting lanthanum salt is soluble, providing free La^{3+} ions. The insoluble lanthanum oxide and hydroxide are not readily peroxidized.

Luminescence spectrum of $^1O_2$: The emission spectrum of $^1O_2$ was recorded for an aqueous solution (H_2O) containing H_2O_2 (5M) and $La(NO_3)_3 \cdot 6H_2O$ (0.5M) at $pH = 9.0$ (Figure 1). The IR emission was detected with a FT-Raman spectrometer in which the laser was switched off. The presence of a well defined emission peak at 1270 nm proves that the decomposition of H_2O_2 by La^{III} generates $^1O_2$ according to Equation (3).

$$2H_2O_2 \xrightarrow[\text{pH=9, 25}\,^\circ\text{C}]{La^{III}} 2H_2O + \alpha\,^1O_2 + (1-\alpha)\,^3O_2 \quad (3)$$

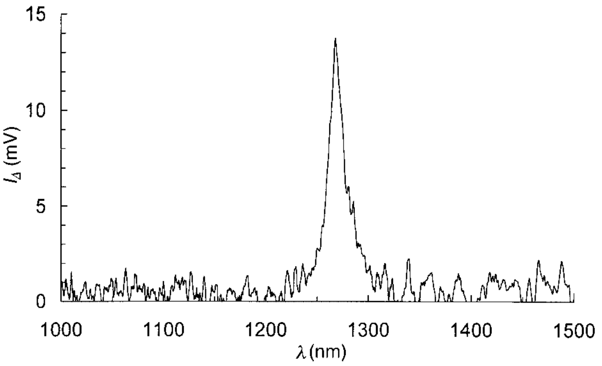


Figure 1. IR spectrum of $^1O_2$ emitted from an aqueous (H_2O) alkaline ($pH = 9.0$) solution containing H_2O_2 (5M) and $La(NO_3)_3 \cdot 6H_2O$ (0.5M) at $T = 25\,^\circ C$.

Optimization and kinetics of the reaction: The decomposition of an aqueous solution of H_2O_2 (0.5M) in the presence of $La(NO_3)_3 \cdot 6H_2O$ (0.1M) at 30 °C was monitored by its IR luminescence at 1270 nm (Figure 2). As soon as NaOH was added, a precipitate appeared at $pH > 4.0$ and a luminescence signal was detected. Under neutral conditions ($pH = 7.0$), a strong luminescence signal, I_Δ, could be obtained (≈ 60 mV) and H_2O_2 was completely decomposed within 15 min.

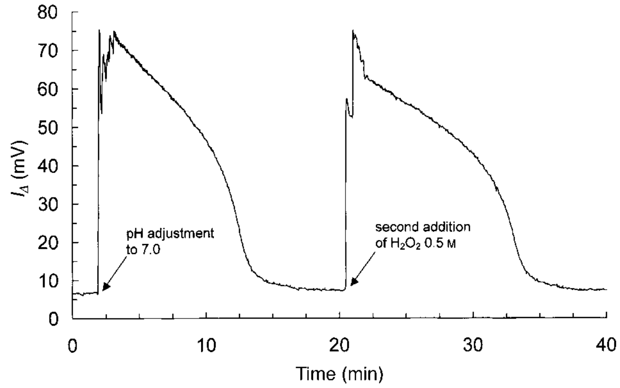


Figure 2. IR luminescence signal I_Δ emitted at 1270 nm by a solution containing $La(NO_3)_3 \cdot 6H_2O$ (0.1M) and H_2O_2 (0.5M) in H_2O at 30 °C and at $pH = 7.0$.

The decay of the IR luminescence signal during the first few minutes may be very rapid, suggesting a transitory state in which peroxidized intermediates are formed at high initial H_2O_2 concentration. The signal then decreases almost linearly, followed by another rapid decrease at the end of the reaction. Simultaneous titration of H_2O_2 with $KMnO_4$ indicates that this rapid decrease in the signal occurs when the H_2O_2/La ratio becomes lower than 2. After about 20 min, a new aliquot of H_2O_2 (0.5M) was added to the reaction medium. A new luminescence signal was then recorded, with exactly the same characteristics as for the first addition of H_2O_2. This result clearly demonstrates that the disproportionation of H_2O_2 by La^{III} is a catalytic process.

To study the influence of the pH on the rate of $^1O_2$ generation by the H_2O_2/La^{III} system, we monitored the intensity of the luminescence signal emitted from aqueous solutions containing $La(NO_3)_3 \cdot 6H_2O$ (0.1M) and H_2O_2 (1.0M) at 25 °C at different pH values. The pH was maintained constant throughout the reaction by addition of small amounts of NaOH (5 M) and/or HCl (2 M). Figure 3 reports the values of the maximum intensities, I_{max}, obtained for the different pH values studied. Values obtained with the well known H_2O_2/MoO_4^{2-} system, conducted under similar experimental conditions, are also shown for comparison.

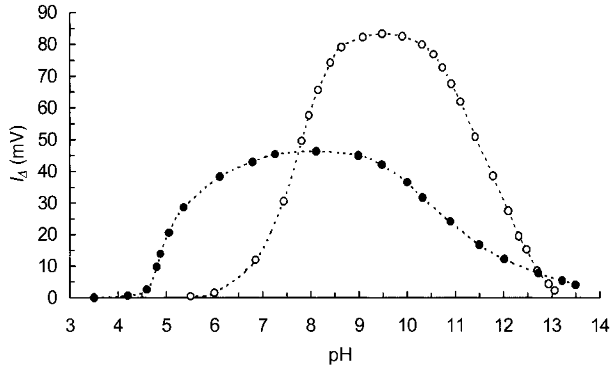


Figure 3. pH dependence of the generation of $^1O_2$ from aqueous solutions containing H_2O_2 (1M) and $La(NO_3)_3 \cdot 6H_2O$ (0.1M) (●) or $Na_2MoO_4 \cdot 2H_2O$ (0.1M) (○) at 25 °C.

As with the systems based on Mo^{VI}, W^{VI}, and Ca^{II},[2, 3, 7, 11] the generation of $^1O_2$ from the La^{III}-catalyzed disproportionation of H_2O_2 exhibits a strong pH dependence with the form of an asymmetrical bell-shaped curve. Nevertheless, the range of pH values at which $^1O_2$ is generated with La^{III} is much larger than that with Mo^{VI}, since a luminescence signal is detected from pH 4.5 to 13.0. In very alkaline media, H_2O_2 dissociates ($pK_a = 11.6$) and the rate of $^1O_2$ formation decreases accordingly. For the system H_2O_2/La^{III}, the pH values for which the rate of $^1O_2$ generation is higher than 90 % of the maximal rate (around pH 8.0) range from 6.5 to 9.5, whereas for the H_2O_2/Mo^{VI} system this pH range is from 8.5 to 10.5. On the other hand, the rate of generation of $^1O_2$ by the H_2O_2/La^{III} system at the optimal pH value under the chosen conditions is apparently 1.8 times lower than for the system H_2O_2/Mo^{VI}, but this point needs to be clarified since the difference could result from a screening effect of the La^{III} particles on the luminescence of $^1O_2$.

Finally, the influence of the H_2O_2 concentration on $^1O_2$ formation was studied by monitoring the luminescence signal emitted from an aqueous alkaline (pH = 9.0) solution containing $La(NO_3)_3 \cdot 6H_2O$ (0.1M) and a starting concentration of H_2O_2 equal to 2 M. Throughout the reaction, the pH was maintained at the value of 9.0. The H_2O_2 was allowed to decompose, and its concentration in the reaction medium was monitored by titration with $KMnO_4$ as soon as the stationary state was reached (after about 2 min). The rate of H_2O_2 decomposition, $d[H_2O_2]/dt$, was then calculated from the curve $[H_2O_2] = f(t)$. Figure 4 reports the luminescence signal (continuous curve) and the rate of H_2O_2 decomposition $d[H_2O_2]/dt$ (black dots) as a function of H_2O_2 concentration.

Figure 4 clearly indicates that at least one equivalent of H_2O_2 is required for $^1O_2$ generation. In addition, we can see that the rate of H_2O_2 disappearance increases uniformly with the concentration of H_2O_2, suggesting that the most peroxidized species is probably the intermediate responsible for the $^1O_2$ generation, in contrast with the Mo^{VI} and W^{VI} catalysts.[3, 8] Similar behavior has already been observed for the system based on Ca^{II}.[7]

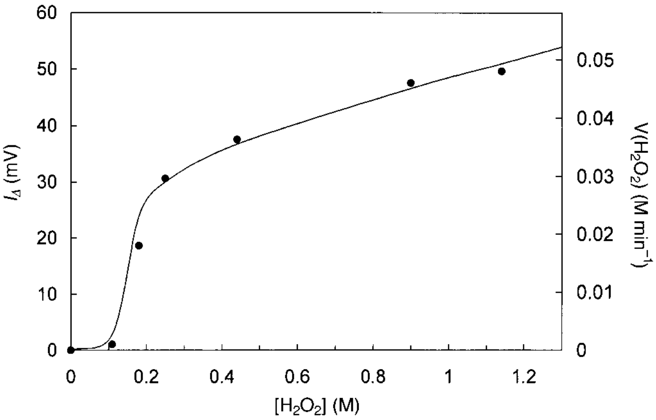
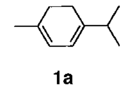


Figure 4. Influence of H_2O_2 concentration on the rate of H_2O_2 decomposition (black dots) and the rate of $^1O_2$ generation (continuous curve). Conditions: $[La(NO_3)_3 \cdot 6H_2O] = 0.1M$, $[H_2O_2]_o = 2M$, H_2O, pH = 9.0, $T = 25\,°C$.

IR luminescence determination of the yield of $^1O_2$ generated from La^{III}/H_2O_2: The $^1O_2$ yield was determined in MeOH by addition of a known amount of α-terpinene (**1a**). This highly reactive chemical trap is known to react with $^1O_2$ by a pure chemical process.[22] Hence, the missing area in the luminescence signal corresponds to the amount of $^1O_2$ trapped by α-terpinene (**1a**). As the total area under the curve is directly related to the cumulative amount of $^1O_2$ generated, comparison of the two areas provides the yield of $^1O_2$, which was found to be equal to 45 ± 5 % for two equivalents of NaOH (Table 2). The yield of $^1O_2$ generation from H_2O_2/La^{III} was also measured in H_2O. As the total area under the curve of the luminescence signal is proportional to the cumulative amount of $^1O_2$ generated, the area of the curve obtained for the H_2O_2/La^{III} system was compared with that obtained for the H_2O_2/Mo^{VI} system under identical conditions. Knowing that $^1O_2$ is generated in a 100 % yield for the H_2O_2/Mo^{VI} system, we were able to deduce that 45 ± 5 % of O_2 generated from the H_2O_2/La^{III} system in water is in the singlet state. This value was confirmed by addition of



1a

Table 2. Determination of the yield of $^1O_2$ generated from H_2O_2/La^{III} in water and methanol by IR luminescence.[a]

Catalyst	Solvent	I_{max} [mV]	t_{end} [min]	Area [mV min^{-1}]	$^1O_2$ Yield [%]
Mo^{VI}	H_2O	55	45	1710	100[2]
La^{III}	H_2O	25	45	765	45[b] 43[c]
La^{III}	CH_3OH	310	40	3025	45

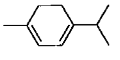
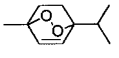
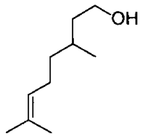
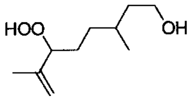
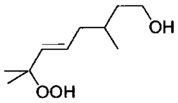
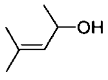
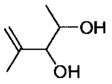
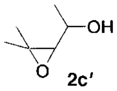
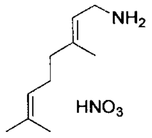
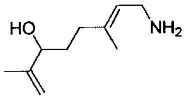
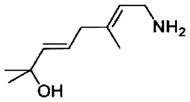
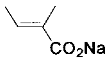
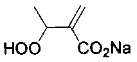
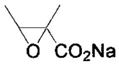
[a] Conditions: [catalyst] = 0.1M, $[H_2O_2]$ = 1M, $T = 25\,°C$, [NaOH] = 0.2M for H_2O_2/La^{III}. [b] By comparison with the area obtained for the system H_2O_2/MoO_4^{2-}. [c] By addition of AES.

a water-soluble trap (anthracene-9,10-bis(ethanesulfonate) or AES; Table 2),[23] by using the method already applied to α-terpinene in MeOH. The yield of $^1O_2$ formation exhibits a pH dependence with a maximum for two equivalents of NaOH.

It is noteworthy that the intensity of the luminescence signal is much higher in methanol than in water. This may be in part explained by the longer lifetime of $^1O_2$ in MeOH ($\tau_\Delta = 10\,\mu s$) than in H_2O ($\tau_\Delta = 4\,\mu s$).

The reason why the yield of $^1O_2$ formation is not 100% remains unclear. There might be two pathways of O_2 formation, one leading to $^1O_2$, the other one to $^3O_2$. Another assumption is that all the oxygen is generated in the singlet state at the surface or inside the heterogeneous catalyst but a part of it may be deactivated into $^3O_2$ by the solid before being released into the solution and only the available $^1O_2$ is detected during the luminescence and trapping experiments.

Table 3. "Dark" singlet oxygenation of alkenes at 30 °C catalyzed by La^{III} or Mo^{VI}.

Entry	Substrate	mmol Substrate mmol H_2O_2 Solvent (mL)	Catalyst (mmol) mmol NaOH	Product(s)	Yield [%] (Selectivity [%])[a]
1	 **1a**	5.0 58.0 MeOH (8)	La (0.15) 0.6	 **2a**	74 (>95)
2	 **1b**	5.0 58.0 MeOH (8)	La (0.15) 0.45	 **2b**  **2b′**	87 (>95) **2b**/**2b′** = 55/45
3		5.0 18 MeOH (8)	Mo (0.15) 0	**2b** + **2b′**	85 (>95) **2b**/**2b′** = 54/46
4	 **1c**	5.0 150 H_2O (2)	La (0.5) 1.5	 **2c**	60[d] (95) *threo*/*erythro* = 1/4
5		0.6 18 D_2O (2)	Mo (0.06) 0	 **2c′**	>95[b] (>95) *threo*/*erythro* = 4/1
6	 **1d**	10.0 71 MeOH[e] (10)	La (0.5) 1.0	 **2d**  **2d′**	53[c,d] (>80) **2d**/**2d′** = 41/59
7		1.0 5.3 D_2O (2)	Mo (0.05) 0	**2d** + **2d′**	<20[b,d] (<20) **2d**/**2d′** = 41/59
8	 **1e**	2.0 30 D_2O (2)	La (0.4) 0.6 (pD = 7.5)	 **2e**  **2e′**	>95[b] (>95) **2e**/**2e′** = 90/10

[a] Selectivity towards isolated product as determined by ^1H NMR analysis of the crude product or reaction mixture. [b] Non-isolated yield as determined by ^1H NMR analysis of the reaction mixture. [c] Yield in 74% pure isolated oil (remainder substrate); pure mixture of products free from substrate obtained in 38% yield after column chromatography. [d] Products obtained after reduction with Na_2SO_3. [e] An NMR-scale experiment with La as catalyst in D_2O resulted in the same singlet oxygenation products as obtained in the preparative experiment in methanol, albeit with somewhat lower selectivity.

La^{III}-catalyzed "dark" singlet oxygenation of alkenes: Some preparative "dark" singlet oxygenations of different types of alkenes have been carried out in order to illustrate the synthetic potential of the La^{III}-based catalyst. Experimental details and results are shown in Table 3. In marked contrast to molybdate-catalyzed peroxidations,[4, 6] careful control of the H_2O_2 addition rate is not required for the lanthanum-catalyzed oxidations. Accordingly, the small-scale experiments of Table 3 were carried out by addition of 50% aqueous H_2O_2 in one portion.[24] In line with the results described above on the efficiency of $^1O_2$ generation in organic solvents, the peroxidation of α-terpinene (**1a**) was found to proceed most efficiently in MeOH (Table 3, entry 1). The selectivity for ascaridole **2a** was found to depend on the absolute amount of the La catalyst and on the molar NaOH/La ratio. Optimum results were obtained with 3 mol% $La(NO_3)_3 \cdot 6H_2O$ and NaOH/La = 4.

The peroxidation of β-citronellol (**1b**) similarly proceeds cleanly in MeOH with NaOH/La = 3 (Table 3, entry 2). The ratio of the expected ene-type singlet oxygenation products—the secondary and tertiary hydroperoxides **2b** and **2b′**—was almost the same as the ratio obtained with $Na_2MoO_4 \cdot 2H_2O$ (Table 3, entry 3). However, significantly less H_2O_2 is required to obtain a high (>90%) conversion with the Mo catalyst than with the La catalyst. This result is in line with the lower percentage of $^1O_2$ formed from H_2O_2 when a La salt is used as the catalyst instead of molybdate, which is known to catalyze H_2O_2 disproportionation with >70% $^1O_2$ generation efficiency in MeOH as solvent.[25]

The metal-catalyzed "dark" singlet oxygenation of allylic alcohols presents a synthetic challenge because of the propensity of allylic alcohols to undergo epoxidation, which proceeds readily under the influence of many metal peroxo species formed in situ from metal salts and H_2O_2.[26] When 4-methyl-pent-3-en-2-ol (**1c**) was subjected to "dark" singlet oxygenation conditions with the $La(NO_3)_3$/NaOH catalyst system in water as the solvent, the product obtained after reduction consisted of 95% 4-methyl-pent-4-ene-2,3-diol (**2c**; *threo*/*erythro* 1:4), as expected for singlet oxygenation of this substrate (Table 3, entry 4).[27] The epoxide **2c′** (*threo*/*erythro* 4:1) corresponded to only ≈5% of the product. In contrast, when Na_2MoO_4 was used in place of $La(NO_3)_3$/NaOH as the catalyst, only epoxidation was observed (Table 3, entry 5).

As well as allylic alcohols, unsaturated amines also present another class of substrates that cannot be subjected to molybdate-catalyzed "dark" singlet oxygenation in alkaline medium. This is because the physical quenching of $^1O_2$ induced by the non-protonated amino group hampers the necessary chemical quenching by the C=C bond and because a non-protonated amino group is sensitive to oxidation. In contrast, when geranylamine (**1d**) was allowed to react in MeOH with an excess of H_2O_2 in the presence of a suspension of the La catalyst ($NaOH/La(NO_3)_3 = 2$), a yellow oil consisting of a mixture of substrate **1d** and two products **2d** and **2d′** in molar ratio **1d**/**2d**/**2d′** 28:29:43 according to GC and ^1H NMR analysis was isolated after reductive workup. Although the two products were readily separated from the substrate by column chromatography, their mutual separation proved to be very difficult. From GC-HRMS in combination with ^1H and ^{13}C NMR data, we conclude that the two products are the two isomeric amino alcohols **2d** and **2d′** (Table 3, entry 6).[28] No evidence of the formation of products derived from attack of $^1O_2$ on the $C{=}CCH_2NH_2$ double bond was obtained. With Na_2MoO_4 instead of $La(NO_3)_3$/NaOH as the catalyst, selectivity towards the desired singlet oxygenation products **2d** and **2d′** is very low (Table 3, entry 7).

Since the La-catalyzed H_2O_2 disproportionation is expected to be influenced by the pH increase resulting from the addition of geranylamine to the H_2O_2-containing La/NaOH catalyst solution, changes in pH resulting from addition of the various components have been determined (Table 4). These pH measurements were carried out in aqueous solution, by use of allylamine as a water-soluble, but considerably less basic analogue of geranylamine (pK_a values of $H_2C{=}CHCH_2NH_2$ and $Me_2C{=}CHCH_2NH_2$ are 9.8 and 10.6 respectively; the pK_a of the latter amine would be expected to be very similar to the pK_a of geranylamine).[29] As can be judged from Table 4, addition of H_2O_2 to the slightly basic $La(NO_3)_3$/NaOH suspension results in a large drop in the pH, which increases again to pH = 9.3 in the final reaction mixture on addition of allyl amine. Because of the significantly higher basicity of geranylamine than of allyl amine, we concluded that the former is almost fully protonated under the reaction conditions. As a result of the electron-withdrawing effect of the allylic $-NH_3^+$ group on the adjacent C=C bond, the attack of electrophilic singlet oxygen is directed to the terminal $Me_2C{=}C$ bond. This explains the high regioselectivity observed in the La-catalyzed "dark" singlet oxygenation of geranylamine in comparison to the Mo-catalyzed one, which occurs in alkaline medium, in which the amino group is non-protonated.

Table 4. pH values of aqueous mixtures containing the various components required for La-catalyzed "dark" singlet oxygenation of allylic amines.

Entry	1	2	3	4
$La(NO_3)_3$ [M]	0.05	0.05	0.05	0.05
NaOH [M]	–	0.10	0.10	0.10
H_2O_2 [M]	–	–	7.0	7.0
allylamine [M]	–	–	–	1.0
pH at 22°C	5.8	8.3	4.3	9.3

Finally, the "dark" singlet oxygenation of sodium tiglate (**1e**) was studied by ^1H NMR spectroscopy in D_2O (Table 3, entry 8). Besides the expected hydroperoxide **2e**, a minor amount (≈10%) of epoxide **2e′** was formed. This was shown by comparison with the reported oxidation of **1e** with Na_2MoO_4 as the catalyst, which also leads to either **2e** or **2e′** as the main product, depending on the pH.[4] It is noteworthy that, on using the La-based system, the amount of epoxide at neutral pH is minimized in relation to the Mo-based system, which provides about 40% of epoxide at this pH value.

Conclusion

The formation of $^1O_2$ by the H_2O_2/La^{III} catalytic system is now unambiguous. In 1985, only the oxide La_2O_3 was studied, but in this work we have shown that the use of a water-soluble lanthanum salt such as $La(NO_3)_3 \cdot xH_2O$ considerably enhances (by about 50-fold) the rate of $^1O_2$ production. In addition, in comparison with known chemical generators of $^1O_2$ based on H_2O_2 disproportionation, this new source of $^1O_2$ presents two main advantages: it is by far the most efficient heterogeneous catalyst and it can generate $^1O_2$ in neutral or even slightly acidic aqueous media, whereas all other known catalysts require alkaline conditions. Probably as a result of the heterogeneous nature of the La catalyst, unfavorable interactions between the metal center and heteroatoms in the substrate are minimized. Accordingly, this new La-system allows catalytic "dark" singlet oxygenation of substrate classes that cannot be peroxidized successfully with the classical Mo-system, such as allylic alcohols or unsaturated amines. Further work to identify the lanthanum peroxides responsible for $^1O_2$ generation is in progress.

Experimental Section

Reagents: Lanthanum oxide La_2O_3 (99.99 %), lanthanum hydroxide $La(OH)_3$ (99.9 %), lanthanum nitrate $La(NO_3)_3 \cdot 6H_2O$ (99.99 %), lanthanum chloride $LaCl_3 \cdot 7H_2O$ (99.9 %), sodium molybdate $Na_2MoO_4 \cdot 2H_2O$ (99 %), sodium hydroxide (99.99 %), geranylamine (90 %), β-citronellol (95 %), α-terpinene (85 %), and tiglic acid (98 %) were purchased from Aldrich Chemie. Hydrogen peroxide (50 % Rectapur) and hydrochloric acid (37 % Normapur) were obtained from Prolabo. 4-Methyl-pent-3-en-2-ol was prepared according to literature procedures[30] and sodium tiglate was obtained from tiglic acid by addition of one equivalent of NaOMe in methanol.

Instrumentation: IR detector: The IR emission of $^1O_2$ was measured with a liquid nitrogen-cooled germanium photodiode detector (Model EO-817L, North Coast Scientific Co., Santa Rosa, CA, USA) sensitive in the spectral region from 800 to 1800 nm, with a 0.25 cm^2 detector and a sapphire window.[31] The emission spectrum of $^1O_2$ was recorded with a calibrated FT-Raman instrument (Bruker FRA 106 FT-Raman module adapted to an IFS 88 FTIR bench; LASIR, USTL, Villeneuve d'Ascq, France) operating with a similar germanium diode detector.

Typical luminescence experiment: An aqueous solution (30 mL H_2O) containing $La(NO_3)_3 \cdot 6H_2O$ (1.7 g, 0.1 M, 4 mmol) was maintained at 25 °C and circulated, with the aid of a peristaltic pump, through a quartz cell positioned in front of the germanium detector. When the background noise of the IR signal was stabilized, H_2O_2 (50 %, 5.7 mL, 2.5 M, 100 mmol) was introduced. The pH was rapidly adjusted to 9.0 by addition of NaOH (5 M) and the total volume of the solution was adjusted to 40 mL by addition of H_2O (3 mL). The pH of the reaction medium was kept constant during the reaction by addition of small amounts of concentrated HCl or NaOH. The intensity of the luminescence signal (I_Δ) was recorded, and simultaneously, 1 mL of the reaction medium was added to H_2SO_4 (10 mL, 1 M), and H_2O_2 was titrated with $KMnO_4$ (0.04 M) to monitor the evolution of the H_2O_2 concentration during the reaction.

Oxidation experiments

Oxidation of *β*-citronellol (1b): A solution of $La(NO_3)_3 \cdot 6H_2O$ (65 mg, 0.15 mmol) and β-citronellol (**1b**, 0.92 mL, 5.0 mmol) in MeOH (8 mL) was warmed to 30 °C, after which aqueous H_2O_2 (50 %, 3.3 mL, 58 mmol) and aqueous NaOH (5 M, 90 μL, 0.45 mmol) were added. A white, milky suspension was formed, and this was stirred overnight at 30 °C. The MeOH was removed on the rotary evaporator and H_2O (30 mL) was added. The white suspension was extracted with Et_2O (5 × 30 mL) and the combined Et_2O layers were dried over Na_2SO_4. After filtration, the Et_2O was removed in vacuum to leave a colorless oil containing the starting material **1b** (7 %) and the two isomers of the hydroperoxides of β-citronellol (**2b**/**2b′** 55:45), according to ^1H NMR spectroscopy. The chemical shifts of the products are in accordance with literature values.[32] Yield: 0.82 g (87 %).

Oxidation of *α*-terpinene (1a): The oxidation of α-terpinene (**1a**, 0.81 mL, 5 mmol) was performed similarly to that of β-citronellol (**1b**), but now with 0.6 mmol of NaOH. A light yellow oil was obtained after workup. ^1H NMR spectroscopy showed this oil to contain ascaridole **2a**, together with 9 % of *p*-cymene (impurity in the α-terpinene starting material). The chemical shifts of the product are in accordance with literature data. Yield: 0.63 g (74 %).[23b]

Oxidation of 4-methyl-pent-3-en-2-ol (1c): A solution of $La(NO_3)_3 \cdot 6H_2O$ (217 mg, 0.5 mmol) in H_2O (2 mL) was warmed to 30 °C, after which aqueous H_2O_2 (50 %, 8.5 mL, 150 mmol), aqueous NaOH (10 M, 150 μL, 1.5 mmol), and 4-methyl-pent-3-en-2-ol (**1c**, 0.51 g, 5 mmol) were added. A white, milky suspension was formed, and this was stirred for 48 h at 30 °C. Na_2SO_3 (5 g, 40 mmol) was added to the mixture. The mixture was stirred for one hour, saturated with NaCl, and extracted with ethyl acetate (5 × 30 mL). The combined organic layers were dried over Na_2SO_4. After filtration, the ethyl acetate was removed in vacuum to afford a colorless oil, containing 4-methyl-pent-4-ene-2,3-diol (**2c**, *erythro*/*threo* 4:1) together with ≈5 % of the epoxide **2c′** (*erythro*/*threo* 1:4). The chemical shifts of the diol and epoxide products are in accordance with literature data.[27b, 33] Yield: 0.36 g (60 %).

Oxidation of geranylamine (1d): A solution of $La(NO_3)_3 \cdot 6H_2O$ (217 mg, 0.5 mmol) in MeOH (5 mL) was warmed to 30 °C, after which aqueous NaOH (10 M, 100 μL, 1.0 mmol) was added. The resulting white suspension was stirred for one minute. After addition of aqueous H_2O_2 (50 %, 4 mL, 71 mmol), a solution of geranylamine (**1d**, 1.85 mL, 10 mmol) and aqueous HNO_3 (65 %, 0.69 mL, 10 mmol) in MeOH (5 mL) was added. The mixture was stirred overnight at 30 °C, during which it turned light yellow. A concentrated aqueous Na_2SO_3 solution (30 mL) was added to the mixture, which was then stirred for one hour, saturated with NaCl, and extracted with ethyl acetate (5 × 50 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was removed on the rotary evaporator to leave a yellow oil (1.21 g). ^1H NMR spectroscopy showed that this oil was a mixture of the substrate **1d**, the two isomers of the product (secondary **2d** and tertiary **2d′** alcohols), and some traces of impurities (ratio according to ^1H NMR: **1d**/**2d**/**2d′** 28:29:43, according to GC: 28:27:45). Separation by column chromatography (eluent: CH_2Cl_2/MeOH/aqueous NH_3 (25 %) 30:5:1) yielded substrate **1d** (0.20 g) as a yellow oil and a light yellow oil (0.65 g) containing the products (mixture of isomers; **2d**/**2d′** 41:59). The assignment of the two isomeric amino alcohols is based on the relative intensities of the signals and on a comparison of the NMR data of the oxidized double bond region with the NMR data of that region in the isomeric products obtained from β-citronellol. Yield: 0.65 g (38 %). $H_2C{=}C(Me)CH(OH)CH_2CH_2C(Me){=}CHCH_2NH_2$ (**2d**): ^1H NMR ($CDCl_3$, 300 MHz, 25 °C): $\delta = 5.22$ (overlap; =CH), 4.88 (s, 1 H; =CHH), 4.77 (s, 1 H; =CHH), 3.97 (t, $J = 6.8$ Hz, 1 H; C*H*OH), 3.22 (overlap; NCH_2), 2.0 (b, 5 H; OH + NH_2 + $=CCH_2$), 1.66 (s, 3 H; CH_3), 1.60 (overlap; C(OH)C*H*$_2$), 1.58 ppm (s, 3 H; CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz, 25 °C): $\delta = 149.4$ (C_{quat}), 137.4 (C_{quat}), 127.7 ($=CH_2$), 112.8 (=CH), 77.1 (HOCH), 41.2 (NCH_2), 37.3 ($=CCH_2$), 34.8 ($HOCCH_2$), 19.4 (CH_3), 18.0 ppm (CH_3).

$Me_2C(OH)CH{=}CHCH_2C(Me){=}CHCH_2NH_2$ (**2d′**): ^1H NMR ($CDCl_3$, 300 MHz, 25 °C): $\delta = 5.4-5.6$ (m, 2 H; C*H*=C*H*), 5.22 (overlap; =CH), 3.22 (overlap; NCH_2), 2.63 (d, $J = 6.4$ Hz, 2 H; $=CCH_2$), 1.59 (s, 3 H; CH_3), 1.25 ppm (s, 6 H; 2 × CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz, 25 °C): $\delta =$ 141.6 (=CH), 138.5 (C_{quat}), 127.2 (=CH), 126.4 (=CH), 72.4 (HOC), 43.9 ($=CCH_2$), 41.2 (NCH_2), 31.6 ($C(CH_3)_2$), 18.0 ppm (CH_3).
HRMS calcd for $[C_{10}H_{20}NO]^+$ 170.1545, found 170.1568.

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