

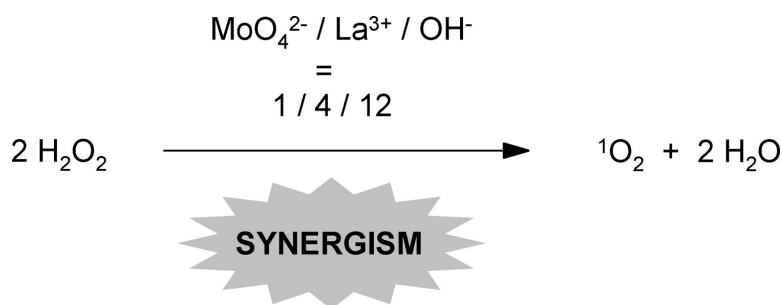
Communication

Synergism between Molybdenum and Lanthanum in the Disproportionation of Hydrogen Peroxide into Singlet Oxygen

Joos Wahlen, Dirk E. De Vos, Marijke H. Groothaert, Vronique Nardello, Jean-Marie Aubry, Paul L. Alsters, and Pierre A. Jacobs

J. Am. Chem. Soc., **2005**, 127 (49), 17166-17167 • DOI: 10.1021/ja0547026 • Publication Date (Web): 16 November 2005

Downloaded from <http://pubs.acs.org> on March 25, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)

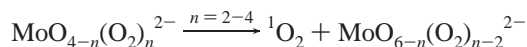
Synergism between Molybdenum and Lanthanum in the Disproportionation of Hydrogen Peroxide into Singlet Oxygen

Joos Wahlen,[†] Dirk E. De Vos,[†] Marijke H. Groothaert,[†] Véronique Nardello,[‡] Jean-Marie Aubry,[‡] Paul L. Alsters,[§] and Pierre A. Jacobs^{*,†}

Centre for Surface Chemistry and Catalysis, Katholieke Universiteit Leuven, 3001 Heverlee, Belgium, LCOM, Equipe de Recherches "Oxydation et Formulation", 59652 Villeneuve d'Ascq Cedex, France, and DSM Pharma Chemicals, Advanced Synthesis, Catalysis and Development, 6160 MD Geleen, The Netherlands

Received July 14, 2005; E-mail: pierre.jacobs@biw.kuleuven.be

Reaction of H₂O₂ with certain metal ions produces peroxy-metal intermediates capable of releasing molecular oxygen in the singlet (¹Δ_g) state.¹ In contrast to triplet (³Σ_g⁻) state oxygen, singlet oxygen (¹O₂) is a reactive yet highly selective oxidant for the peroxidation of olefinic compounds.² In particular, molybdate (MoO₄²⁻) is an efficient catalyst for the disproportionation of H₂O₂ into ¹O₂. Both the mechanism³ and the synthetic utility⁴ have been investigated. In aqueous alkaline media, Mo and H₂O₂ form a series of mononuclear peroxy species, [MoO_{4-n}(O₂)_n]²⁻ (n = 1–4). Of these, especially oxotriperoxy-Mo (n = 3), releases ¹O₂ at a high rate, while tetraperoxy-Mo is far more stable:



This means that the reaction rate decreases at high [H₂O₂]; hence, fast disproportionation requires gradual addition of H₂O₂ over time. The H₂O₂ concentration not only affects the rate but also the selectivity of the reaction; at high [H₂O₂] direct oxygen-atom transfer from tetraperoxy-Mo becomes competitive with ¹O₂ formation, resulting in the formation of unwanted epoxide products.⁵ To overcome these drawbacks, we reasoned that by adding other peroxy-forming metals to Mo, the stability of the peroxy-Mo species might be influenced in such a way that the dependence of the rate and selectivity on [H₂O₂] is altered and that higher catalytic activities are attainable.

Various peroxy-forming metals were screened as cocatalysts for Na₂MoO₄ in the disproportionation of H₂O₂ at high initial [H₂O₂] (3 M in methanol, Mo/H₂O₂ = 1/2000). Addition of lanthanum(III) nitrate, another ¹O₂-generating catalyst,⁵ led to a strong increase of the overall activity compared to the monometallic Mo or La catalysts (Figure 1). The combination of other peroxy-forming metals with Mo or La gave no or only small rate enhancements (Figure S1, Supporting Information). Control experiments established the essential role of both Mo and La in the improved catalytic turnover (Figure S1). Similar rate enhancements were observed in other solvents such as water and acetonitrile. Even under nonoptimized conditions (Mo/La/NaOH = 1/4/20), the overall turnover frequency (TOF, based on Mo+La) is 219 h⁻¹. In the same conditions, the individual TOF for Mo and La are 4 and 31 h⁻¹, respectively. The low activity of Mo is due to the high [H₂O₂], promoting the formation of stable tetraperoxy-Mo. The maximum activity of Mo under optimum conditions of low [H₂O₂] has been reported to be 36 h⁻¹.³

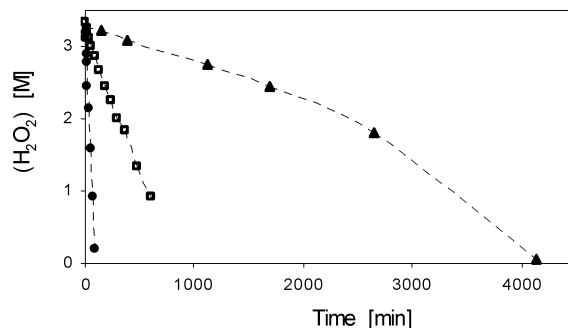


Figure 1. H₂O₂ disproportionation catalyzed by Mo (▲), La (□), and the combined action of Mo and La (●). Conditions: 0.1 mmol Mo, 0.1 mmol La, or 0.02 mmol Mo and 0.08 mmol La, and 0.4 mmol NaOH and 40 mmol H₂O₂ (50 wt %) were stirred (700 rpm) at 25 °C in 10 mL of methanol. H₂O₂ determination by cerimetry.

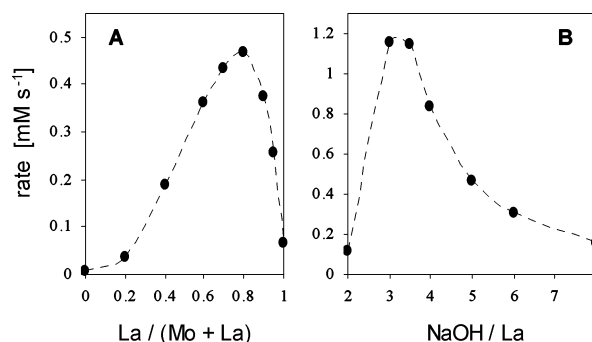


Figure 2. Influence of the La/Mo (A) and NaOH/La (B) ratios on the rate of H₂O₂ disproportionation. Conditions A: x mmol La, (0.1 – x) mmol Mo, 0.4 mmol NaOH and 40 mmol H₂O₂ were stirred (700 rpm) at 25 °C in 10 mL of methanol. B: 0.08 mmol La, 0.02 mmol Mo, and x mmol NaOH.

The initial rates of H₂O₂ disproportionation were determined for different Mo/La/NaOH combinations, keeping the total amount of metal at 0.1 mmol. As shown in Figure 2A, at constant [NaOH], the reaction rate strongly depends on the Mo/La ratio, an optimum being observed at a Mo/La molar ratio of 1/4. These data clearly show a synergistic effect between Mo and La.⁶ The amount of NaOH also has a profound influence on the activity of Mo and La. This was studied by varying [NaOH] at a constant Mo/La ratio of 1/4 (Figure 2B). A well-defined maximum is observed at a NaOH/La ratio of 3/1. Under optimized conditions (Mo/La/NaOH = 1/4/12), the overall TOF amounts to 546 h⁻¹.

Most likely, the NaOH/La optimum is related to the hydrolysis of La³⁺, yielding partially (NaOH/La < 3/1) or fully hydrolyzed La species, La(OH)₃.⁷ In systems with only La, it is believed that the insoluble La hydroxide is catalytically active, while partially hydrolyzed La shows much lower activity.⁵ The Mo/La ratio of

[†] Katholieke Universiteit Leuven.

[‡] LCOM.

[§] DSM Pharma Chemicals.

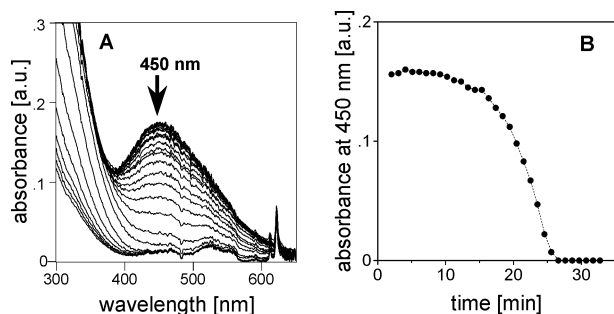


Figure 3. UV-vis spectral changes at 1 min intervals (A) and time course of the disappearance of $\text{Mo}(\text{O}_2)_4^{2-}$ (B) during the disproportionation of H_2O_2 catalyzed by Mo and La. $[\text{H}_2\text{O}_2]_0$ is 1.65 instead of 3 M in Figure 1.

1/4 is not readily interpreted on a molecular level. This optimum may well reflect the maximum number of favorable interactions between soluble peroxy-Mo anions and accessible La sites on the surface of the solid La hydroxide.⁸

Convincing evidence for the production of singlet ($^1\Delta_g$) oxygen was obtained by detection of the near-infrared (1270 nm) chemiluminescence accompanying the radiative decay of $^1\text{O}_2$ (Figure S2).^{3b} This experiment confirms the very high $^1\text{O}_2$ flux generated from Mo-La. The H_2O_2 efficiency of the various Mo/La/NaOH combinations was assessed by chemical trapping of the formed $^1\text{O}_2$ with citronellol. This alkene contains two distinct allylic hydrogen atoms and reacts with $^1\text{O}_2$ to yield an equimolar mixture of allylic hydroperoxides. At constant $[\text{NaOH}]$, all Mo-La combinations show H_2O_2 efficiencies around 40% with 100% hydroperoxide selectivity (Figure S3, Table S1). Notably, the H_2O_2 efficiency of La in the absence of Mo is only 20% at complete H_2O_2 consumption (24 h). Mo itself shows higher efficiency (>50%), but the activity is very low. More than 70 h are required to achieve full H_2O_2 conversion, and the hydroperoxide selectivity is only 70% due to competitive epoxidation by tetraperoxy-Mo.

The exact reason for the nonlinear catalytic behavior displayed by Mo and La is difficult to assess. Visual inspection of the reaction medium showed no permanent adsorption of the colored peroxy-Mo species on the white La hydroxide.⁹ In situ UV-vis DRS spectroscopy showed that a major part of Mo is present as red-brown $\text{Mo}(\text{O}_2)_4^{2-}$ (Figure 3A). The concentration of this species only slightly decreases during the experiment, except at very low $[\text{H}_2\text{O}_2]$ (Figure 3B). Similar spectra were obtained in the presence of Al instead of La, but in this case, the H_2O_2 disproportionation was very slow (Figure S4).

As to the individual metals, reaction of H_2O_2 with Mo results in the formation of anionic η^2 -peroxy complexes.³ La, on the other hand, has been reported to react with H_2O_2 via a μ -peroxy coordination mode.^{5,10–12} Possibly, in the present system, peroxide-

linked complexes are formed between Mo and La. These complexes might possess lower stability than the individual peroxy-metal species, resulting in their fast disproportionation.

In conclusion, the cooperative action between Mo and La leads to a unique catalyst system that combines high turnover rates with improved selectivity toward the formation of $^1\text{O}_2$.

Acknowledgment. This work was supported by the European Commission (SUSTOX project, G1RD-CT-2000-00347) and the Belgian Government (IUAP project on Supramolecular Catalysis).

Supporting Information Available: Experimental details, Figures S1–S4 and Table S1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Aubry, J. M. *J. Am. Chem. Soc.* **1985**, *107*, 5844–5849.
- (2) (a) Wahlen, J.; De Vos, D. E.; Jacobs, P. A.; Alsters, P. L. *Adv. Synth. Catal.* **2004**, *346*, 152–164. (b) Clennan, E. L.; Pace, A. *Tetrahedron* **2005**, *61*, 6665–6691.
- (3) (a) Aubry, J. M.; Cazin, B. *Inorg. Chem.* **1988**, *27*, 2013–2014. (b) Böhme, K.; Brauer, H.-D. *Inorg. Chem.* **1992**, *31*, 3468–3471. (c) Niu, Q. J.; Foote, C. S. *Inorg. Chem.* **1992**, *31*, 3472–3476. (d) Nardello, V.; Marko, J.; Vermeersch, G.; Aubry, J. M. *Inorg. Chem.* **1995**, *34*, 4950–4957. (e) Arab, M.; Bougeard, D.; Aubry, J. M.; Marko, J.; Paul, J. F.; Payen, E. *J. Raman Spectrosc.* **2002**, *33*, 390–396.
- (4) (a) Aubry, J.-M.; Bouttemy, S. *J. Am. Chem. Soc.* **1997**, *119*, 5286–5294. (b) Nardello, V.; Bogaert, S.; Alsters, P. L.; Aubry, J.-M. *Tetrahedron Lett.* **2002**, *43*, 8731–8734. (c) Nardello, V.; Caron, L.; Aubry, J.-M.; Bouttemy, S.; Wirth, T.; Saha-Möller, C.; Adam, W. *J. Am. Chem. Soc.* **2004**, *126*, 10692–10700.
- (5) Nardello, V.; Barbillat, J.; Marko, J.; Witte, P. T.; Alsters, P. L.; Aubry, J.-M. *Chem. Eur. J.* **2003**, *9*, 435–441.
- (6) The combined application of several metals, leading to regio-, chemo-, or stereoselectivity and/or activity that differs significantly from a strictly additive effect, is often referred to as synergism. For example, see: Li, C.; Widjaja, E.; Garland, M. *J. Am. Chem. Soc.* **2003**, *125*, 5540–5548.
- (7) Baes, C. F., Jr.; Mesmer, R. E. *The Hydrolysis of Cations*; Wiley-Interscience: New York, 1976; pp 129–146.
- (8) No detailed kinetic analysis was carried out because of the inherent complexity of the system. Moreover, since La occurs as an ill-defined hydroxide gel, unambiguous identification of the catalytically active species is extremely difficult, if at all possible.
- (9) Polyoxometalate anions bind lanthanide cations to form materials with extended metal-oxygen frameworks. In contrast to the alkaline pH used in this work, these coordination complexes are typically formed at acidic to neutral pH. For example, see: Peacock, R. D.; Weakley, T. J. R. *J. Chem. Soc. A* **1971**, 1836–1839.
- (10) For isolated peroxy-lanthanide complexes, see: (a) Bradley, D. C.; Ghotra, J. S.; Hart, F. A.; Hursthouse, M. B.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1974**, 40–41. (b) Djordjevic, C.; Vuletic, N. *Inorg. Chem.* **1980**, *19*, 3049–3053. (c) Barnes, J. C.; Blyth, C. S.; Knowles, D. *Inorg. Chim. Acta* **1987**, *126*, L3–L6.
- (11) La and H_2O_2 show high phosphodiester cleavage activity. For example, see: Takasaki, B. K.; Chin, J. *J. Am. Chem. Soc.* **1995**, *117*, 8582–8585.
- (12) La complexes and *tert*-butyl hydroperoxide are used for the asymmetric epoxidation of enones. For example, see: Nemoto, T.; Ohshima, T.; Yamaguchi, K.; Shibasaki, M. *J. Am. Chem. Soc.* **2001**, *123*, 2725–2732.

JA0547026