

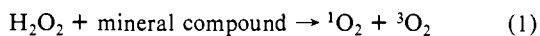
Search for Singlet Oxygen in the Decomposition of Hydrogen Peroxide by Mineral Compounds in Aqueous Solutions

J. M. Aubry

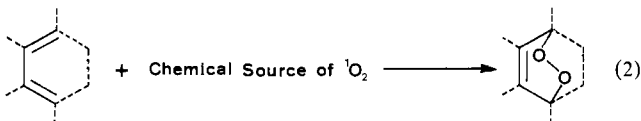
Contribution from the Laboratoire de Chimie Générale, Faculté de Pharmacie de Lille, 59045 Lille Cédex, France. Received March 26, 1985

Abstract: The possibility of singlet oxygen ($^1\text{O}_2$) occurrence in the decomposition of H_2O_2 by mineral compounds in aqueous basic solutions was examined. Tetrapotassium rubrene-2,3,8,9-tetracarboxylate was used as a trap, giving an endoperoxide detected by HPLC. We found that four families of mineral compounds lead to the formation of the endoperoxide: the oxides of the alkaline earths Ca, Sr, and Ba; the derivatives of elements of groups 3A, 4A, 5A, and 6A in d^0 configuration (except niobium); the oxides of actinides and lanthanides; and finally the oxidizers ClO^- , BrO^- , Au^{3+} , IO_3^- , and IO_4^- . One compound in each family was selected for further investigation in order to strengthen the $^1\text{O}_2$ hypothesis. Thus, the yield of the endoperoxide of tetrapotassium 9,10-diphenylanthracene-2,3,6,7-tetracarboxylate was enhanced when the parent compound was introduced in a mixture of $\text{H}_2\text{O}_2 + (\text{ClO}^-, \text{Nd}_2\text{O}_3, \text{MoO}_4^{2-}, \text{Ca}(\text{OH})_2) +$ deuterated water instead of light water.

Since the historical discovery by Khan and Kasha in 1963 of the generation of singlet oxygen, $^1\text{O}_2$, in the oxidation of H_2O_2 by ClO^- ,¹ several other chemical sources of $^1\text{O}_2$ have been found.² Mineral peroxidic compounds are frequently involved in these processes, either in the oxidation (ClO^- ,¹ BrO^-)³ or in the disproportionation (CeO_2 ,⁴ MoO_4^{2-} ,⁵ OH^- ,⁶ $\text{Fe}(\text{II})$)⁷ of H_2O_2 itself (reaction 1) or in the decomposition of peroxy-metal species (K_3CrO_8 ,^{8,9} CrO_5 ,¹⁰ $\text{Ph}_3(\text{Br})\text{SbOOSb}(\text{Br})\text{Ph}_3$)¹¹ prepared from H_2O_2 .



In some cases (ClO^- ,^{1,9} BrO^- ,^{3,9} CeO_2 ,⁴ K_3CrO_8 ,^{8,9} $\text{Fe}(\text{II})$)⁷ $^1\text{O}_2$ involvement was firmly established by spectroscopic, trapping, and kinetic studies. With $\text{Ph}_3(\text{Br})\text{SbOOSb}(\text{Br})\text{Ph}_3$,^{11a} $^1\text{O}_2$ formation seems also likely, since an endoperoxide is produced when this peroxide reacts with a conjugated diene (reaction 2); however,



endoperoxides of some *nonaromatic dienes* can also be prepared by a nonsinglet oxygen mechanism.¹² In the other cases (MoO_4^{2-} , OH^- , CrO_5)^{10b} reports are more questionable. Up to now, no general rule for the formation of $^1\text{O}_2$ could be sifted out from these scattered results; thus, we undertook a systematic screening of

the periodic classification searching for $^1\text{O}_2$ in the decomposition of aqueous H_2O_2 induced by mineral compounds. As the pH of the solution is an important parameter for this process, the medium was buffered with NaOH to minimize the acido-basic effects of the tested mineral compounds. Sodium hydroxide was chosen to avoid side reactions which could have occurred between H_2O_2 and common buffers and also because alkaline solution favors the formation of metallic peroxides.^{13,14} Singlet oxygen generated in these processes was measured quantitatively by trapping agents; most of the traps used were water-soluble derivatives of aromatic compounds which are relatively unreactive toward the mineral peroxides but which lead to well-defined endoperoxides with $^1\text{O}_2$. The results point out the effect of various mineral compounds on the formation of these endoperoxides in an aqueous basic solution of hydrogen peroxide, and the discussion is based on the assumption that $^1\text{O}_2$ is involved in these peroxidations.

Results

Screening of the Periodic Classification. The possible singlet oxygen generated by the decomposition of hydrogen peroxide was trapped with a water-soluble rubrene derivative, tetrapotassium rubrene-2,3,8,9-tetracarboxylate¹⁵ (RTC). This red compound is very soluble in neutral or basic water and exhibits high reactivity toward $^1\text{O}_2$, yielding only the colorless endoperoxide RTCO_2 ¹⁵ (Figure 1). As fading of RTC could also occur with some other oxidizing agents, the reacting mixtures were analyzed by HPLC for RTCO_2 which is considered to be specific of $^1\text{O}_2$ involvement. The concentration of this endoperoxide was inferred from the area of the corresponding peak compared with a standard solution obtained by self-sensitized photooxygenation of RTC. Analyses were carried out after 24 h because it was observed that self-disproportionation of H_2O_2 in our basic medium was achieved after this time; however, with many mineral compounds, H_2O_2 disappears completely within 1 h. The formulas of tested mineral compounds are classified in Table I in four parts, according to their ability to generate the endoperoxide RTCO_2 . These compounds were generally oxides, hydroxides, or oxoanions in order to avoid possible interference of ligands; their concentrations (2×10^{-2} M) were high enough to measure easily a $^1\text{O}_2$ yield as low as 1%.

The results obtained with RTC suggest $^1\text{O}_2$ involvement in the decomposition of H_2O_2 with a wide variety of compounds; however, the method may be criticized at three levels.

(1) The identification of the endoperoxide RTCO_2 by HPLC is ambiguous as RTC could be oxidized into another product having the same retention time as RTCO_2 .

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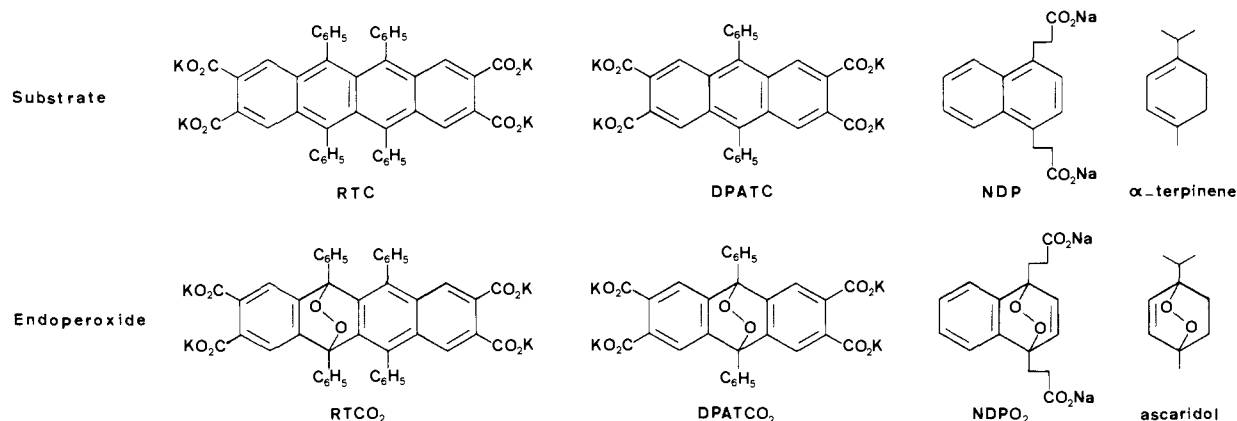
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Table I. RTCO_2 Yields ($=[\text{RTCO}_2]_{\infty}/[\text{RTC}]_0$) after 24 h for the Oxidation of RTC in an Aqueous Mixture of H_2O_2 (10^{-1} M), NaOH (10^{-1} M) and a Mineral Compound (2×10^{-2} M)^a

yield \geq 70 %	10% \leq yield < 70%	yield < 10%	yield \sim 0		
Ca(2) = $\text{Ca}(\text{OH})_2$	Sr(2) = $(\text{Sr}(\text{OH})_2)$	Nb(5) = Nb_2O_5	H(1) = H_2O	Li(1) = $\text{LiOH}, \text{H}_2\text{O}$	Na(1) = NaOH
Sc(3) = Sc_2O_3	Ba(2) = $(\text{Ba}(\text{OH})_2)$	Zn(2) = ZnO	K(1) = KOH	Rb(1) = RbCl	Cs(1) = CsNO_3
La(3) = La_2O_3	Y(3) = Y_2O_3	Cd(2) = $\text{Cd}(\text{OH})_2$	Be(2) = $\text{Be}(\text{OH})_2$	Mg(2) = MgO	Cr(3) = Cr_2O_3
Ti(4) = H_2TiO_3	Zr(4) = ZrO_2	Ga(3) = Ga_2O_3	Mn(3) = $\text{Mn}_2\text{O}_3, x\text{H}_2\text{O}$	Mn(4) = MnO_2	Mn(6) = K_2MnO_4
Zr(4) = $\text{ZrO}(\text{NO}_3)_2, x\text{H}_2\text{O}$	Hf(4) = HfO_2	Ir(4) = IrCl_4	Mn(7) = KMnO_4	Re(7) = KReO_4	Fe(2) = $(\text{FeSO}_4, 7\text{H}_2\text{O})$
V(5) = NaVO_3	Ta(5) = Ta_2O_5	Ge(4) = GeO_2	Fe(3) = Fe_2O_3	Ru(3) = (RuCl_3)	Ru(4) = $\text{RuO}_2, x\text{H}_2\text{O}$
Mo(6) = $\text{Na}_2\text{MoO}_4, 2\text{H}_2\text{O}$	Cr(6) = K_2CrO_4	Bi(3) = Bi_2O_3	Os(8) = (OsO_4)	Co(2) = $(\text{Co}(\text{NO}_3)_2, 6\text{H}_2\text{O})$	Co(3) = Co_2O_3
W(6) = $\text{Na}_2\text{WO}_4, 2\text{H}_2\text{O}$	Au(3) = (AuCl_3)	Te(6) = $\text{K}_2\text{TeO}_4, x\text{H}_2\text{O}$	Rh(3) = $(\text{RhCl}_3, 3\text{H}_2\text{O})$	Ni(2) = NiO	Ni(3) = Ni_2O_3
Pr(3+4) = Pr_6O_{11}	Ce(4) = CeO_2		Pd(2) = $\text{Pd}(\text{OH})_2$	Pt(4) = PtO_2	Cu(1) = Cu_2O
Nd(3) = Nd_2O_3	Gd(3) = Gd_2O_3		Cu(2) = CuO	Ag(1) = Ag_2O	Hg(1) = $\text{Hg}_2(\text{NO}_3)_2$
Sm(3) = Sm_2O_3	U(6) = $(\text{NH}_4)_2\text{U}_2\text{O}_7$		Hg(2) = HgO	B(3) = $\text{Na}_2\text{B}_4\text{O}_7$	Al(3) = $\text{Al}_2(\text{OH})_6$
Eu(3) = Eu_2O_3	I(5) = (KIO_3)		In(3) = (InCl_3)	Tl(1) = (TlNO_3)	Tl(3) = Tl_2O_3
Dy(3) = Dy_2O_3	I(7) = (NaIO_4)		C(4) = Na_2CO_3	Si(4) = $\text{Na}_2\text{SiO}_3, 5\text{H}_2\text{O}$	Sn(2) = $\text{SnO}, x\text{H}_2\text{O}$
Er(3) = Er_2O_3	Tm(3) = Tm_2O_3		Sn(4) = SnO_2	Pb(2) = PbO	Pb(4) = PbO_2
Yb(3) = Yb_2O_3			N(3) = NaNO_2	N(5) = NaNO_3	P(1) = $\text{NaH}_2\text{PO}_2, \text{H}_2\text{O}$
Th(4) = ThO_2			P(3) = $\text{Na}_2\text{HPO}_3, 5\text{H}_2\text{O}$	P(5) = Na_2HPO_4	As(3) = NaAsO_2
Cl(1) = NaClO			As(5) = $\text{Na}_2\text{HASO}_4, 7\text{H}_2\text{O}$	Sb(3) = Sb_2O_3	Sb(5) = $\text{KSb}(\text{OH})_6$
Br(1) = NaBrO			Bi(5) = NaBiO_3	O(-1/2) = KO_2	O(-1) = H_2O_2
Tb(3+4) = Tb_4O_7			S(4) = Na_2SO_3	S(6) = Na_2SO_4	Se(4) = $\text{Na}_2\text{SeO}_3, 5\text{H}_2\text{O}$
Ho(3) = Ho_2O_3			Se(6) = $\text{H}_2\text{SeO}_4, 2\text{H}_2\text{O}$	F(-1) = NaF	Cl(-1) = NaCl
Lu(3) = Lu_2O_3			Cl(3) = $\text{NaClO}_2, \text{H}_2\text{O}$	Cl(5) = KClO_3	Cl(7) = $\text{NaClO}_4, \text{H}_2\text{O}$
			Br(-1) = $\text{NaBr}, 2\text{H}_2\text{O}$	Br(5) = NaBrO_3	I(-1) = NaI

^a When a compound brought about a side reaction, its formula is shown in parentheses.**Figure 1.** Formulas of $^1\text{O}_2$ traps and endoperoxides used to study the decomposition of H_2O_2 induced by mineral compounds in basic water.

(2) RTCO_2 could be produced by a nonsinglet oxygen mechanism since formation of the endoperoxide of rubrene itself has been suggested to occur via the action of ClO^- or O_3 on rubrene;¹⁶ however, these suggestions have never been proven thoroughly.¹⁷ Moreover, in the case of the water-soluble rubrene derivative, RTC, it was shown in preceding works that $^3\text{O}_2$, H_2O_2 , and O_2^- do not react with RTC and that the powerful oxidizers HO^\cdot , ClO^- and O_3 produce a bleaching of RTC but the oxidation products do not contain the endoperoxide RTCO_2 .^{9,15,18} Thus the detection of RTCO_2 can be considered as rather convincing evidence of $^1\text{O}_2$ involvement in an unknown process. However, the possibility that an intermediary metallic peroxide could mimic $^1\text{O}_2$ reactivity cannot be completely ruled out.

(3) RTC itself could be a key intermediate for $^1\text{O}_2$ generation through the oxidation of its carboxylic functions into peracids followed by a disproportionation of the latter.^{3,19} Finally, we selected one typical compound in each family identified in the discussion part (ClO^- , Nd_2O_3 , MoO_4^{2-} , $\text{Ca}(\text{OH})_2$) for complementary investigations.

Table II. Effect of Various Additives on the Formation of NDPO_2 in the Reaction of H_2O_2 with NDP in Aqueous Basic Solution

	mineral compound				
	ClO^-	Nd_2O_3	MoO_4^{2-}	$\text{Ca}(\text{OH})_2$	none
mineral compd (M)	1.5×10^{-1}	5×10^{-1}	10^{-2}	5×10^{-1}	
% NDPO_2	20	22	58	80	0
$^1\text{O}_2$ yield (%) ^a	22	7	1040	48	0
	3	4	10	24	0

^a Yields based on the concentration of the mineral compounds (first line); yields based on the initial concentration of H_2O_2 (second line).

Formation of a Thermodynamically Unstable Endoperoxide. Disodium 3,3'-(1,4-naphthylidene)dipropionate (NDP) reacts slowly ($\beta = 0.16$ M)²⁰ with $^1\text{O}_2$, producing an unstable endoperoxide NDPO_2 which gives back NDP upon heating as do the other derivatives of 1,4-dimethylnaphthalene²¹ (Figure 1). Therefore, this highly water-soluble trap is suitable for checking the efficiency of new $^1\text{O}_2$ sources and for proving the formation of an endoperoxide by

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Table III. Deuterium Solvent Effect on the Chemical Peroxidation of DPATC

	mineral compound			
	ClO ⁻	Nd ₂ O ₃	MoO ₄ ²⁻ ^a	Ca(OH) ₂
DPATCO ₂ in H ₂ O (%)	19	7	33	45
¹ O ₂ yield (%) ^b	27	10	52	78
	5	2	21	16
DPATCO ₂ in D ₂ O (%)	32	62	72	85
isotopic purity of D ₂ O (%)	92.1	98.5	98.5	98.5
β _{H₂O} /β _{D₂O} exptl	1.9	5.5	3.2	5
calcd	7	11	11	11

^a[H₂O₂] = 5 × 10⁻² M was used instead of 0.1 M to lower % DPATCO₂ in H₂O. ^bYield based on the mineral compound concentration (first line); yield based on the initial H₂O₂ concentration (second line).

a single HPLC analysis. The experimental procedure already described for RTC was used, but, considering the low reactivity of NDP and the instability of NDPO₂ even at room temperature, more concentrated reagents were added and reaction times were shortened (see Experimental Section). Results are reported in Table II. At the end of the reaction time, the mixture was heated at 50 °C for 1 h to regenerate NDP.

The detection by HPLC of a product with the same retention time as an authentic sample of NDPO₂ suggested heavily the formation of this endoperoxide during the decomposition of H₂O₂. This assumption was confirmed unambiguously by the regeneration of the trap after warming the aqueous phase 1 h at 50 °C.

Deuterium Solvent Effect. The formation of an endoperoxide of a polycyclic aromatic compound during an oxidation process is already a telling test for ¹O₂ involvement; however, it is useful to strengthen the ¹O₂ hypothesis with another test. One of the most peculiar properties of ¹O₂ is the deuterium solvent effect; it was observed that the ¹O₂ lifetime, τ, is much longer in a deuterated solvent than in a protonated one.²² In water, experimental determinations of the ratio τ_{D₂O}/τ_{H₂O} vary from 10^{2.2a} to 17.²³ Hence, if a chemical trap of ¹O₂ is introduced into an aqueous solution at a concentration well below β and submitted to a ¹O₂ source, we should observe, at least, a 10-fold enhancement for the rate of reaction when D₂O is used instead of H₂O. Such an experiment was carried out with another ¹O₂ trap, the tetrapotassium 9,10-diphenylanthracene-2,3,6,7-tetracarboxylate (DPATC, Figure 1). This compound is less reactive (β = 2.6 × 10⁻² M)⁹ than RTC toward ¹O₂ and it reacts only partly under the experimental conditions already used for RTC. So it is suitable for checking the accelerating effect of D₂O. Table III reports the yields of endoperoxide DPATCO₂ obtained in light or heavy water; it shows an important deuterium effect in agreement with the ¹O₂ hypothesis.

Peroxidation of α-Terpinene. Singlet oxygen traps used in preceding experiments have always been added at a low concentration compared with mineral reagents. However, their water-solubilizing groups COO⁻ could be involved in ¹O₂ generation by the following catalytic process; some peroxide would oxidize carboxylate anions into peracid functions by an unknown reaction; the latter would disproportionate in the basic solution giving oxygen and the starting carboxylic functions. It is known that about 70% of the oxygen produced by this reaction is in the singlet state.¹⁹

To rule out this possibility, a singlet oxygen trap without water-solubilizing groups, α-terpinene, was tried. It reacts rapidly (β = 3 × 10⁻³ M in CH₃OH)²⁴ with ¹O₂, giving an endoperoxide, ascaridol (Figure 1), but considering the low solubility of these compounds in pure water, a mixed solvent, CH₃OH/H₂O, 70:30,

Table IV. Effect of Various Additives on the Formation of Ascaridol in the Reaction of H₂O₂ with α-Terpinene in a Basic Mixture of CH₃OH/H₂O, 70:30^a

	mineral compound				
	ClO ⁻	Nd ₂ O ₃	MoO ₄ ²⁻	Ca(OH) ₂	none
reaction time		7 h	30 min	7 h	7 h
% ascaridol	90	65	80	65	0
% α-terpinene	0	2	0	4	90

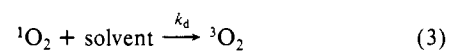
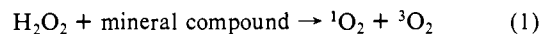
^aYields are calculated from HPLC chromatograms.

was used. The ascaridol was generally identified by HPLC by comparison with an authentic sample; in the case of MoO₄²⁻ the formation of the endoperoxide was confirmed by its ¹H NMR and IR spectra because several mineral compounds complicate the chromatogram. The yields of ascaridol and the ratio of unchanged α-terpinene are reported in Table IV.

In a control experiment, it was shown that H₂O₂ in basic solutions leaves the α-terpinene almost unchanged after 7 h at room temperature. On the contrary, when one of the selected mineral compounds was added, the trap disappeared and ascaridol was produced in good yields.

Discussion

Formation of the endoperoxides was tentatively interpreted in terms of ¹O₂ involvement according to the following kinetics (A = substrate, AO₂ = endoperoxide) assuming that quenching is negligible with our traps.



Under stationary conditions, processes 1, 3, and 4 lead to the following equation for the rate of the disappearance of A.

$$\frac{d[A]}{dt} = - \left(\frac{d[{}^1\text{O}_2]}{dt} \right) \frac{k_r[A]}{k_d + k_r[A]}$$

where (d[¹O₂]/dt)_g is the rate of ¹O₂ generation. Integration of this equation between t₀ and t_∞ (end of the reaction time) gives²⁴ [A]_∞ = [A]₀ - [A]_∞ + β ln ([A]₀/[A]_∞), where [A]₀ and [A]_∞ are the concentrations of A at the beginning and at the end of the reaction, β = k_d/k_r, and [A]_∞ is the total amount of ¹O₂ generated chemically between t₀ and t_∞. Considering that H₂O₂ is always present in large excess, the ¹O₂ yield for reaction 1 is generally based on the concentration C of the mineral compound under study, assuming a complete solubility in the medium ([¹O₂]_∞ = C(¹O₂ yield)). When no secondary reaction occurs, [A]₀ = [A]_∞ + [AO₂]_∞. Under our conditions ([A]₀ - [A]_∞) << β ln ([A]₀/[A]_∞), except for α-terpinene, thus

$${}^1\text{O}_2 \text{ yield} = \frac{\beta}{C} \ln ([A]_0/[A]_\infty) = \frac{\beta}{C} \ln (1 + [\text{AO}_2]_\infty/[A]_\infty) \quad (5)$$

The concentrations [A]₀, [A]_∞, and [AO₂]_∞ are inferred from the area of each peak of the chromatograms compared with standard solutions.

Comparison of the Mineral Compounds. Results of the screening experiments quoted in Table I allowed us to estimate the ability of the tested mineral compounds to generate ¹O₂ in presence of aqueous basic H₂O₂. Singlet oxygen yields were calculated from eq 5 knowing the Foote reactivity index of RTC (β = 1.5 × 10⁻³ M)²³ and the concentration of the mineral reagent (C = 2 × 10⁻² M). Results are summarized in a periodic classification (Figure 2) with the following conventions: if no derivative of a chemical element has been studied, the corresponding rectangle is left empty; if some derivatives of an element have been investigated, the oxidation numbers of compounds which produce a significant quantity of ¹O₂ (>1%) are printed above the chemical symbol and the others below; if a side reaction occurs, such as precipitation

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H 1																			
Li 1	Be 2											B 3	C 4	N 3.5	O 2, -1, -1.0	F -1			
Na 1	Mg 2											Al 3	Si 4	P 1.3.5	S 4.6	Cl -1, 3.5, 7			
K 1	Ca 2	Sc 3	Ti 4	V 5	Cr 6 3	Mn 3, 4, 6, 7	Fe (2), 3	Co (2), 3	Ni 2, 3	Cu 1, 2	Zn 2	Ga 3	Ge 4	As 3.5	Se 4, 6	Br -1, 5			
Rb 1	Sr (2)	Y 3	Zr 4	Nb 5	Mo 6		Ru (3), 4	Rh (3)	Pd 2	Ag 1	Cd 2	In (3)	Sn 2, 4	Sb 3, 5	Te 6	I (5), 7			
Cs 1	Ba (2)	La 3	Hf 4	Ta 5	W 6	Re 7	Os (6)	Ir 4	Pt 4	Au (3)	Hg 1, 2	Tl (1), 3	Pb 2, 4	Bi 3, 5					
			Ce 4	Pr 3+4	Nd 3		Sm 3	Eu 3	Gd 3		Tb 3+4	Dy 3	Ho 3	Er 3	Tm 3	Yb 3	Lu 3		
			Th 4		U 6 4														

Figure 2. Classification of the mineral compounds according to their ability to generate ¹O₂ in the presence of aqueous basic H₂O₂.

of a salt between RTC and a metallic cation (Ba²⁺, Fe²⁺, ...), or degradation of the tetracenic core (OsO₄, IO₄⁻, ...), the oxidation number is bracketed; when the ratio [RTCO₂]_∞/[RTC]₀ lies in the intervals [0–10]%, [10–70]%, [70–100]%, corresponding to ¹O₂ yields of [0–1]%, [1–10]%, [10–100]%, the backgrounds of the rectangles are respectively white, lined, or black.

In this table, we did not distinguish between compounds which do not give any RTCO₂ (O₂⁻,¹⁸ H₂O₂, OH⁻, Sb₂O₃, ...) and those (Bi₂O₃, Cd(OH)₂, Nb₂O₅, ...) which lead to the formation of minute amounts of endoperoxide (0 < [RTCO₂]_∞/[RTC]₀ < 10%) since this very low ¹O₂ production (<1%) could be due to impurities. However, some of these doubtful compounds could become efficient ¹O₂ generators under different experimental conditions (pH, temperature,⁶ concentrations, ligands,¹¹ or physical structure of the mineral reagent⁴). Among the compounds which produce a significant quantity of ¹O₂ [1–100%], we find, of course, ClO⁻ and BrO⁻ but also MoO₄²⁻,⁵ CeO₂,⁴ CrO₄²⁻,^{8,9} and many other unsuspected compounds which can be classified into four families: (1) oxidizing compounds (ClO⁻, BrO⁻, Au³⁺, IO₃⁻, IO₄⁻); (2) oxides of lanthanides and actinides; (3) oxides of transition elements of groups 3A, 4A, 5A, and 6A in d⁰ configuration, except niobium which leads only to the formation of traces of RTCO₂; and (4) hydroxides of the alkaline-earths Ca, Sr, and Ba.

Up to now, little is known about the mechanism of ¹O₂ generation; only rough thermodynamic considerations can be drawn from the comparison of the values of "standard" potentials at pH 13 (*E*^o). At this pH, *E*^o for the couple O₂/HO₂⁻ is -0.05 V if O₂ is in the ground state and 0.44 V if O₂ is in the first singlet state ¹Δ_g. Thus, the oxidizing agents whose "standard" potentials are higher than 0.44 V should be able to oxidize H₂O₂ into singlet oxygen with a low activation energy. In the same way, if *E*^o lies between -0.05 and 0.44 V, ¹O₂ could be generated also, but the reaction would occur with a significant activation energy as a part of it will be necessary for the formation of ¹O₂.²⁵ "Standard" potentials at pH 13 for all common oxidation states of chemical elements can be determined from Pourbaix's potential-pH diagrams.²⁶ If we take into account only mineral compounds yielding

more than 1% of ¹O₂ (first two columns of Table 1), six of them belong to redox couples with *E*^o > 0.44 V (ox/red, *E*^o(V): ClO⁻/Cl⁻, 0.95; BrO⁻/Br⁻, 0.82; CeO₂/Ce(OH)₃, 0.78; Au(OH)₃/Au, 0.67; IO₅³⁻/IO₃⁻, 0.68; PrO₂/Pr(OH)₃, 0.65) and for two of them -0.05 V < *E*^o < 0.44 V (IO₃⁻/I⁻, 0.32; CrO₄²⁻/Cr(OH)₃, -0.03).

On the contrary, if *E*^o is lower than -0.05 V, the corresponding compound will not be able to oxidize H₂O₂ directly and will have to be "activated" with, at least, another molecule of H₂O₂. In this case, ¹O₂ formation would result from a more or less intricate disproportionation of the peroxide bridge; this could even happen without a change in the oxidation number of the metal. Indeed, CrO₄²⁻ in alkaline solution reacts with H₂O₂ according to this scheme, although *E*^o for the couple CrO₄²⁻/Cr(OH)₃ is slightly higher than -0.05 V. Thus a number of authors have reported that the net reaction is a disproportionation of H₂O₂ via the formation of tetraperoxychromate(V) with complete regeneration of the starting chromate.²⁷ Molybdate and tungstate anions behave similarly although it seems that the oxidation states of the metals remain equal to VI for the intermediary peroxy complexes.²⁸ Broadly speaking, it appears that all metallic compounds of the first two columns of Table I (except Au(III)) are known to produce relatively stable peroxy complexes with H₂O₂.^{13,14} This fact suggests that the key step for ¹O₂ generation could involve the reaction of coordinated peroxy groups instead of free hydrogen peroxide. Only a careful study of each metal would permit the identification of this key step, the understanding of the mechanism, and the improvement of ¹O₂ yield.

Trapping of ¹O₂ with NDP. All the selected mineral compounds led to high yields of RTCO₂ in the screening experiments. On the contrary, with NDP (β = 0.16 M) and under much more drastic conditions, yields of NDPO₂ vary only from 20 to 80% (Table II) because NDP is less reactive by a factor of ~100 than RTC toward ¹O₂. However, these results must be compared cautiously as the thermal instability of NDPO₂ at room tem-

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perature forced us to stop the reaction before complete decay of H_2O_2 . According to Table II, $\text{Ca}(\text{OH})_2$ appeared to be the most efficient compound to produce NDPO_2 within a short time in aqueous solution; thus the system $\text{Ca}(\text{OH})_2/\text{H}_2\text{O}_2$ could be a useful alternative to the photooxygenation process to peroxidize $^1\text{O}_2$ carriers such as NDP.

Assuming that $^1\text{O}_2$ is the reactive species, its yield, based on the mineral compound added, was calculated from eq 5 and reported in Table II. For ClO^- we found a yield of 22% although it is known that $^1\text{O}_2$ is generated quantitatively under these conditions.²⁹ This discrepancy arises from our dosing method which can measure only the singlet oxygen produced in solution and not the gaseous one. In fact, Khan and Kasha have proven that a part of $^1\text{O}_2$ is generated in the gas phase;³⁰ moreover, the ratio of gaseous $^1\text{O}_2$ increases with the reagent concentration and the $\text{ClO}^-/\text{H}_2\text{O}_2$ reaction is now used as a gaseous $^1\text{O}_2$ source for chemically pumped iodine lasers.³¹ On the other hand, the $^1\text{O}_2$ yield is much higher than 100% with molybdate, a result in accord with a catalytic behavior of MoO_4^{2-} ; in this case the $^1\text{O}_2$ yield must be calculated with respect to the initial concentration of H_2O_2 .

Accelerating Effect of D_2O . From results reported in Table III the experimental ratios $\beta_{\text{H}_2\text{O}}/\beta_{\text{D}_2\text{O}}$ were determined assuming that $^1\text{O}_2$ yields are the same in H_2O and D_2O (eq 5). If k_r (reaction 4) has the same value in D_2O and H_2O , the theoretical ratio $\beta_{\text{H}_2\text{O}}/\beta_{\text{D}_2\text{O}}$ can be calculated taking into account the isotopic purity of D_2O ²⁴ and the known isotopic effect on $^1\text{O}_2$ lifetime $\tau_{\text{D}_2\text{O}}/\tau_{\text{H}_2\text{O}} = 13$.³²

The experimental ratios show large isotopic effects, though lower than the calculated ones, even for the reaction $\text{ClO}^- + \text{H}_2\text{O}_2$ which is a well-known source of $^1\text{O}_2$. A lower yield of $^1\text{O}_2$ in D_2O than in H_2O could account for this discrepancy. Indeed, from Table III, it appears that more than 80% of H_2O_2 disproportionates by a nonsinglet oxygen pathway; if $^1\text{O}_2$ generation occurs through one or several O-H cleavage, a slackening effect of D_2O is expected owing to the higher stability of the O-D bond. On the contrary, the rate of other pathways without hydrogen transfer would undergo little change. Thus in D_2O , more H_2O_2 would be decomposed by these nonsinglet mechanisms. Hence, Kajiwara and Kearns³³ have observed that the singlet oxygen production rate is smaller in D_2O than in H_2O when ClO^- oxidizes H_2O_2 , and that the kinetics is more intricate in D_2O . However, for this latter reaction, another difficulty arises from our experimental procedure, as a concentrated solution (0.3 M) of ClO^- in H_2O had to be mixed with the solution of H_2O_2 0.1 M in D_2O . A part of $^1\text{O}_2$ is generated before complete homogenization and is quenched more efficiently in this protonated environment than in the homogeneous solution. Botsivali and Evans¹⁹ found a higher isotopic effect than ours for the same reaction ($\beta_{\text{H}_2\text{O}}/\beta_{\text{D}_2\text{O}} = 6$), but they probably used more dilute solutions of ClO^- and H_2O_2 as their $^1\text{O}_2$ trap is six times more reactive than DPATC.

Influence of the Carboxylate Groups on $^1\text{O}_2$ Generation. The hydrophobic trap, α -terpinene, was oxidized into ascaridol when the selected mineral compounds were stirred with a solution of hydrogen peroxide in the mixed solvent methanol/water (Table IV). Thus, carboxylic groups are not necessary for the generation of the endoperoxide. Furthermore, the formation of ascaridol through the reaction of the cation radical of α -terpinene with triplet oxygen¹² is unlikely since such a carbocation would react immediately with OH^- ions of the solution.

Addition of methanol to the medium slackened all the reactions under study. In the case of ClO^- , this effect is favorable since less $^1\text{O}_2$ escaped in the gas phase. With MoO_4^{2-} , the rate is still convenient, as the oxidation of α -terpinene reached completion within 30 min leading to the formation of 80% ascaridol; in this

process MoO_4^{2-} seems also to act as a catalyst since a concentration of 5×10^{-3} M is sufficient to oxidize 10^{-2} M α -terpinene with regeneration of the molybdate after complete disproportionation of H_2O_2 . On the other hand, the rate-retarding effect is more pronounced for Nd_2O_3 and $\text{Ca}(\text{OH})_2$, as a reaction time of 7 h is needed to oxidize most of the starting compound, giving a less satisfactory yield of ascaridol. The secondary reactions could proceed from the decomposition of the trap and its endoperoxide by the mineral peroxides according to the known high reactivity of nonaromatic conjugated dienes and their endoperoxides.³⁴ These side reactions could limit usefulness of these new peroxidation methods for frail substrates.

Conclusions

Our studies of the decomposition of H_2O_2 in basic water initiated by mineral compounds suggest heavily that singlet oxygen is generated with a wide variety of compounds. These results have both theoretical and practical implications in several fields.

(a) The study of the spectroscopic state of oxygen is a new approach to the investigation of H_2O_2 decomposition. This method does not disturb the mechanism and can afford a further insight into the evolution of electronic distribution in the peroxide bond during the reaction. From this point of view, it is complementary to the use of O^{18} as a tracer which can detect the conservation or the cleavage of the O-O bond.³⁵ From our work it appears that besides the current mechanism involving the radical species O_2^- and OH^- ,³⁶ another pathway leading to $^1\text{O}_2$ can also occur through the decomposition of metallic peroxides.

(b) These new mineral $^1\text{O}_2$ generators could be useful in organic synthesis, either directly if the organic molecule does not react with the metallic peroxide itself³⁷ or via a singlet oxygen carrier. In the same way, if $^1\text{O}_2$ can be extracted in the gas phase in good yield, some of these processes could provide interesting alternatives to the reaction $\text{ClO}^- + \text{H}_2\text{O}_2$ as sources of $^1\text{O}_2$ for chemically pumped iodine lasers.³¹

Experimental Section (See Figure 1)

Reagents. Commercial α -terpinene (Aldrich), stabilizer-free hydrogen peroxide (30%, Merck, Perhydrol Suprapur), sodium hydroxide 1-hydrate (NaOH , H_2O , Merck, Suprapur), and deuterium oxide (99.7% D_2O , Aldrich) were used without further purification. Aqueous solutions of sodium hypochlorite (NaClO , Rectapur), neodymium oxide (Nd_2O_3 , >99.9%), sodium molybdate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, Puriss p.a.), calcium hydroxide ($\text{Ca}(\text{OH})_2$, Rectapur) were respectively purchased from Prolabo, Pechiney, Fluka, and Prolabo. Other mineral compounds had the highest purity available from Prolabo, Aldrich, or Koch-Light. Rose Bengal immobilized on hydrophilic polymer (Sensitox II) was a generous gift of Professor A. Paul Schaap.

Synthesis. Tetrapotassium rubrene-2,3,8,9-tetracarboxylate (RTC),¹⁵ its endoperoxide (RTC_2),¹⁵ tetrapotassium 9,10-diphenylanthracene-2,3,6,7-tetracarboxylate (DPATC),³⁸ and disodium 3,3'-(1,4-naphthylidene)dipropionate (NDP)³⁹⁻⁴¹ were prepared according to known procedures. Ascaridol was prepared by photooxygenation of α -terpinene in a methanolic suspension of Sensitox II.

Endoperoxide of Tetrapotassium 9,10-Diphenylanthracene-2,3,6,7-tetracarboxylate (DPATC₂). A few drops of a concentrated solution of hematoporphyrin in ethanol were added to a solution of tetramethyl 9,10-diphenylanthracene-2,3,6,7-tetracarboxylate⁴² (40 mg) in 10 mL of chloroform (stored on Na_2CO_3). This solution was irradiated at 15 °C with a 500-W mercury high-pressure lamp (Philips SP500) using a filter (GG 475, Schott) and maintaining a continuous bubbling of oxygen, until constant absorbance at 397 nm (after 1/100e dilution) was recorded (1

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h 30 min). Removal of the solvent and washing with methanol provided the endoperoxide of the tetraester (31 mg, 71%) as white crystals. A solution of this compound (31 mg) in warm dioxane (1 mL) was mixed with 1 M KOH in methanol (5 mL) and refluxed for 30 min. The precipitate was collected and washed with methanol (2 mL) leading to the endoperoxide of the tetrapotassium salt, DPATCO₂ (30 mg, 83%).

Endoperoxide of Disodium 3,3'-(1,4-Naphthylidene)dipropionate (NDPO₂). Sensitox II (100 mg) was added to a solution of NDP (1 g) in water (0.5 mL) and methanol (9.5 mL). This mixture was irradiated for 3 h at 5 °C under stirring, with a 500-W mercury high-pressure lamp (Philips SP 500) using a filter (GG 515, Schott) and maintaining a continuous bubbling of oxygen. The sensitizer was filtered off and washed with chilled methanol (20 mL, 0 °C). The resulting solution was dried by stirring at 0 °C with Na₂SO₄ (2 g) during 15 min. After filtration, cold ether (60 mL, 0 °C) was added to the solution and stirred 10 min to induce precipitation of the endoperoxide NDPO₂. The precipitate was collected and dried 2 h in vacuo (0.1 torr, 0 °C) yielding NDPO₂ (850 mg, 80%) as a white powder. HPLC analysis showed 95% of NDPO₂, 4% starting material, and about 1% of secondary products. Solid NDPO₂ is quite stable at -20 °C.

Instrumentation. Analyses of the reaction products were carried out by HPLC (Varian 8500, column lichrosorb RP 18) using a mixture of H₂O/C₂H₅OH/H₃PO₄ as eluent (280/320/1 for RTC, 330/270/1 for DPATC and NDP, 150/450/0 for α -terpinene), and UV detection (260 nm for RTC, 233 nm for DPATC, 210 nm for NDP and α -terpinene) was performed with a variable-wavelength monitor (Spectromonitor III, Sopares). The IR spectrum of ascaridol was recorded on a Perkin-Elmer 297 spectrophotometer. The nuclear magnetic resonance spectrum (¹H NMR) of ascaridol was obtained on a Varian EM 390 spectrometer.

Screening of the Periodic Classification. A mixture of 1 mL of H₂O, 100 μ mol of NaOH (10⁻¹ M), 100 μ mol of H₂O₂ (10⁻¹ M), and 0.2 μ mol (2 \times 10⁻⁴ M) of RTC was stirred in the dark, at room temperature for 24 h with 20 μ mol (2 \times 10⁻² M) of the mineral compound under study. The disappearance of RTC and appearance of RTCO₂ were monitored by HPLC after 1 h and 24 h.

Formation a Thermodissociable Endoperoxide. A mixture of 1 mL of H₂O, 100 μ mol of NaOH (10⁻¹ M), 1 mmol of H₂O₂ (1 M), and 5 μ mol (5 \times 10⁻³ M) of NDP was stirred at room temperature with the mineral compound under study (mineral compound/concentration/reaction time: ClO⁻/1.5 \times 10⁻¹ M/5 min, Nd₂O₃/5 \times 10⁻¹ M/3 h, MoO₄²⁻/10⁻² M/3 h, Ca(OH)₂/5 \times 10⁻¹ M/1 h). The disappearance of NDP and appearance of NDPO₂ were monitored by HPLC. At the end of the reaction, the mixture was centrifuged and the liquid was warmed 1 h at 50 °C to regenerate NDP from NDPO₂.

Deuterium Solvent Effect. A solution of 10 μ L of DPATC 10⁻² M in D₂O (2 \times 10⁻⁴ M), 25 μ L of NaOH 2 M in D₂O (10⁻¹ M), 2.5 μ L (MoO₄²⁻), or 5 μ L (ClO⁻, Nd₂O₃, Ca(OH)₂) of H₂O₂ 30% in H₂O (5 \times 10⁻² M or 10⁻¹ M) was mixed with H₂O or D₂O in order to obtain a final volume of 500 μ L. Then 10 μ mol (2 \times 10⁻² M) of the mineral compound was added with stirring. The disappearance of DPATC and appearance of DPATCO₂ were monitored by HPLC after 15 h.

Peroxidation of α -Terpinene. Analytical Scale. A mixture of 0.75 mL of H₂O (30%), 1.75 mL of CH₃OH (70%), 250 μ mol of NaOH (10⁻¹ M, except for Ca(OH)₂), 500 μ mol of H₂O₂ (2 \times 10⁻¹ M), and 25 μ mol of α -terpinene (10⁻² M) was stirred at room temperature with the mineral compound under study (mineral compound/concentration/reaction time: ClO⁻/7 \times 10⁻² M/1 h, Nd₂O₃/5 \times 10⁻² M/7 h, Na₂MoO₄/10⁻² M/30 min, Ca(OH)₂/5 \times 10⁻² M/7 h). Under these conditions, HPLC analysis showed that most of the α -terpinene had disappeared and that the corresponding endoperoxide (ascaridol) was produced in addition to secondary products.

Preparative Scale. A mixture of 8 mmol of H₂O₂ (2 \times 10⁻¹ M), 4 mmol of NaOH (10⁻¹ M), 0.4 mmol of Na₂MoO₄ (10⁻² M), and 0.8 mmol of α -terpinene (110 mg, 2 \times 10⁻² M) was introduced into 40 mL of a mixed solvent, CH₃OH/H₂O, 70:30. The composition of the red-brown homogeneous solution was monitored by HPLC. After 30 min at room temperature the solution had faded to a light yellow color, α -terpinene had completely disappeared, and a product with the same retention time as ascaridol had emerged. Water (50 mL) was added and the mixture was extracted with ether (4 \times 50 mL). The ethereal layer was washed with water (20 mL) and dried with MgSO₄. Evaporation yielded an oil (70 mg) which showed the same ¹H NMR and IR spectra as an authentic sample of ascaridol prepared by photooxygenation.

Note Added in Proof. A recent paper of Evans agrees with our finding of ¹O₂ generation in the reaction H₂O₂ + IO₄⁻.⁴³

Registry No. RTC, 78034-60-3; RTCO₂, 78075-92-0; DPATC, 83687-18-7; DPATCO₂, 97826-16-9; NDP, 97860-58-7; NDPO₂, 97860-59-8; Sensitox II, 94035-43-5; O₂, 7782-44-7; H₂O₂, 7722-84-1; CaO, 1305-78-8; SrO, 1314-11-0; BaO, 1304-28-5; ClO⁻, 14380-61-1; BrO⁻, 14380-62-2; Au³⁺, 16065-91-1; IO₃⁻, 15454-31-6; IO₄⁻, 15056-35-6; Nd₂O₃, 1313-97-9; MoO₄²⁻, 14259-85-9; Ca(OH)₂, 1305-62-0; D₂O, 7789-20-0; Sc₂O₃, 12060-08-1; La₂O₃, 1312-81-8; H₂TiO₃, 12026-28-7; ZrO(NO₃)₂, 13826-66-9; NaVO₃, 13718-26-8; Na₂WO₄, 13472-45-2; Na₂MoO₄, 7631-95-0; Pr₆O₁₁, 12037-29-5; Sm₂O₃, 12060-58-1; Eu₂O₃, 1308-96-9; Dy₂O₃, 1308-87-8; Er₂O₃, 1314-37-0; Yb₂O₃, 12061-16-4; ThO₂, 1314-20-1; NaClO, 7681-52-9; NaBrO, 13824-96-9; Tb₄O₇, 12037-01-3; Ho₂O₃, 12055-62-8; Lu₂O₃, 12032-20-1; Sr(OH)₂, 18480-07-4; Ba(OH)₂, 17194-00-2; Y₂O₃, 1314-36-9; ZrO₂, 1314-23-4; HfO₂, 12055-23-1; Ta₂O₅, 1314-61-0; K₂CrO₄, 7789-00-6; AuCl₃, 13453-07-1; CeO₂, 1306-38-3; Gd₂O₃, 12064-62-9; (NH₄)₂U₂O₇, 7783-22-4; KIO₃, 7758-05-6; NaIO₄, 7790-28-5; Tm₂O₃, 12036-44-1; Nb₂O₅, 1313-96-8; ZnO, 1314-13-2; Cd(OH)₂, 21041-95-2; Ga₂O₃, 12024-21-4; IrCl₄, 10025-97-5; GeO₂, 1310-53-8; Bi₂O₃, 1304-76-3; K₂TeO₄, 15571-91-2; α -terpinene, 99-86-5; ascaridol, 512-85-6; methanol, 67-56-1; hematoporphyrin, 14459-29-1; 9,10-diphenyl-2,3,6,7-tetra(methoxy-carbonyl)anthracene endoperoxide, 97860-60-1.

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A Theoretical Study of Model Substituted Phosphoranes, PH₄X: Apicophilicities, Geometries, and Electron Densities

Robert S. McDowell[†] and Andrew Streitwieser, Jr.*

Contribution from the Department of Chemistry, University of California, Berkeley, California 94720. Received September 4, 1984

Abstract: The relative energies of model apically and equatorially substituted phosphoranes, PH₄X, are calculated for both standard and fully optimized structures. The resulting order of ligand apicophilicity is Cl > CN > F > CCH > H > CH₃ > OH > O⁻ > S⁻ > NH₂ > BH₂. Apicophilicity is enhanced by ligand electronegativity and diminished by π donation; the effects of these σ and π interactions on the remaining PH₄ moiety and the concomitant geometrical changes resulting from incorporation of the substituent into the phosphorane system are examined using electron density analysis. We conclude from this analysis that d-functions on phosphorus are important in bonding to the apical ligands.

Displacement reactions of tetracoordinate phosphorus, including phosphate ester hydrolysis and the Wittig reaction, proceed by

means of metastable trigonal-bipyramidal intermediates, with the attacking and leaving groups occupying apical positions.¹ Nu-