^{95}Mo NMR and Kinetic Studies of Peroxomolybdic Intermediates Involved in the Catalytic Disproportionation of Hydrogen Peroxide by Molybdate Ions

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The mono-, di-, tri- and tetraperoxomolybdate intermediates formed in the reaction between molybdate ions and hydrogen peroxide are identified by ^{95}Mo NMR. The influences of pH and hydrogen peroxide concentration are discussed in terms of equilibrium constants. Comparison of these results with kinetic studies, performed under the same conditions, leads us to conclude that the oxotriperoxomolybdate $MoO(O_2)_3^{2-}$ is the main precursor of molecular oxygen. The decomposition rates of the different intermediates are also determined, and a mechanistic scheme is proposed.

Introduction

In 1963, Khan and Kasha discovered that the reaction between hypochlorite ions and hydrogen peroxide produces molecular oxygen in an excited singlet state ($^1O_2$, $^1\Delta_g$).[1] Fifteen years later, Held et al. showed that the formation of $^1O_2$ in this process is quantitative.[2] This kind of reaction, which can likewise take place with BrO^-,[3] occurs through H_2O_2 oxidation. Since that time, several other chemical sources of $^1O_2$ have been found.[4] Aubry undertook a systematic screening of the periodic classification by bringing about the decomposition of aqueous alkaline H_2O_2 solution with a wide variety of mineral oxides, hydroxides, or oxoanions.[5] The possible generated $^1O_2$ was detected by a specific water-soluble trap. About 30 new chemical sources of singlet oxygen were discovered. In most cases, the process resulted from a disproportionation rather than from an oxidation of H_2O_2.

The hydrogen peroxide/molybdate ions system has been investigated in details as the reaction proceeds in a homogeneous phase and efficiently generates $^1O_2$ at room temperature (eq 1).

$$2H_2O_2 \xrightarrow{MoO_4^{2-}} 2H_2O + {}^1O_2 \quad (100\%) \qquad (1)$$

Evidence for the formation of singlet oxygen was obtained unambiguously by different methods: (i) specific chemical trapping of $^1O_2$ with tetrapotassium rubrene-2,3,8,9-tetracarboxylate (RTC),[6] (ii) detection of the IR luminescence of $^1O_2$ at 1270 nm,[7,8] and (iii) the deuterium solvent effect which takes advantage that the lifetime of $^1O_2$ is 15 times longer in D_2O than in H_2O.[6−8]

In this process, MoO_4^{2-} acts as a catalyst and singlet oxygen yield is quantitative. The rate of $^1O_2$ formation, which strongly depends upon pH and concentration of H_2O_2, is maximum at pH 10.5.[6] The disproportionation of H_2O_2 by MoO_4^{2-} was studied for a long time by many authors following the pioneering work of Spitalsky and Funck[9] in 1927. All these works suggested the involvement of several intermediates, i.e. mono-, di-, tri- and tetraperoxo complexes.[10−12]

Csanyi[12−14] established the equilibria which occur in dilute acid, neutral, and alkaline solutions and reported stability and acidity constants for the peroxo complexes. Some of these species have been isolated in the solid state. Stomberg determined by X-ray analysis the crystal structures of the red tetraperoxomolybdate anion $Mo(O_2)_4^{2-}$,[15] of the yellow dimeric tetraperoxodimolybdate anion $[Mo_2O_3(O_2)_4(H_2O)_2]^{2-}$,[16] and of many other polynuclear peroxomolybdates.[11,17−20] More recently, Campbell et al.[21] supplemented Raman studies by using ^{95}Mo NMR spectroscopy in order to determine the nature of the different species formed in aqueous solution of H_2O_2/MoO_4^{2-} in the range of $0.5 \leq pH \leq 8.8$.

In spite of all these investigations, the nature of the precursor of singlet oxygen is still a matter of controversy. On the basis of kinetic and UV spectroscopy studies, Aubry and Cazin proposed the dioxodiperoxomolybdate(VI) anion ($MoO_2(O_2)_2^{2-}$) as the species responsible for the formation of $^1O_2$.[6] Unfortunately, UV spectroscopy does not allow an unambiguous characterization of the mono-, di-, and triperoxomolybdates which have close absorption bands. In a later report, Niu and Foote concluded that $Mo(O_2)_4^{2-}$ could also be an important precursor of singlet oxygen in the decomposition of H_2O_2.[8]

The aim of the present work is to reinvestigate the disproportionation of hydrogen peroxide by the molybdate ions, at high concentrations. ^{95}Mo NMR was used in order to get direct

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evidence for the different species formed in neutral and alkaline media, with different concentrations of H_2O_2 and pH values. The results are related to the kinetics of the disproportionation of H_2O_2, and a mechanistic scheme is proposed.

Experimental Section

Materials. NMR Studies. Sodium molybdate dihydrate (99%) and sodium hydroxide (99.995%) were from Aldrich Chemie. Hydrogen peroxide (50% Rectapur) was from Prolabo, Paris. Deuterium oxide (99.8% D) was from CEA (Commissariat à l'Energie Atomique, Saclay, France). Potassium tetraperoxodimolybdate ($K_2[Mo_2O_3(O_2)_4]\cdot 4H_2O$)[22] and sodium tetraperoxomolybdate ($Na_2Mo(O_2)_4\cdot 4H_2O$)[23] were prepared according to known procedures.

Kinetic Studies. Reagents of the highest purity commercially available were used. Sodium molybdate dihydrate and ultrapure sodium hydroxide hydrate were purchased from Johnson Matthey GmbH Puratronic. Stabilizer-free hydrogen peroxide (30% Perhydrol Suprapure) was from Merck. Milli Q (Millipore) water was used. The latter was pretreated by deionization and was passed through a $QPAK_2$ purification pack. This pack consisted of a 0.5 μm prefilter, active coal, an ion-exchange resin of nuclear quality, and an Organex-Q blending. The conductance of the resulting water was 18.2 S. Titration of hydrogen peroxide was carried out by a standard 1 N solution of potassium permanganate (Titrinorm, Prolabo).

Instrumentation. UV/Visible Spectrophotometry. Data were obtained with a Milton Roy Spectronic 3000 spectrophotometer equipped with a diode array photodetector. Full-wavelength scanning measurements can be obtained almost instantaneously, and the detection wavelengths are reliable.

^{95}Mo NMR. The natural abundance ^{95}Mo NMR spectra were recorded at 19.56 MHz using a Bruker AC 300P FT-spectrometer (Laboratoire d'Applications RMN, Université de Lille II) with 10-mm nonspinning sample tubes. The probe temperature was regulated at 273 ± 1 K, except for overnight spectra which were run at room temperature. All chemical shifts were referenced to a $Na_2MoO_4\cdot 2H_2O$ solution (2 M) in D_2O (pH = 11) by the replacement technique. The errors in measuring the chemical shifts were ±2 ppm for a line width below 150 Hz, ±5 ppm for a line width in the range 200−500 Hz, and ±10 ppm for a line width over 500 Hz. Typical data acquisition parameters were as follows: sweep width 21 740 Hz, 4 K data points, resolution 10.6 Hz per point. Each sample contained 20% (v/v) D_2O for field frequency lock. In order to reduce the effects of probe ringing, the Belton sequence from the Bruker Automation program Library for Aspect 3000 computer was used (25.3 μs for a 90° pulse).[24] A 80 μs preacquisition delay was introduced. A line-broadening factor of 100 Hz was applied before Fourier transformation. Each spectrum represents an average of 768 scans (about 5 min duration) unless otherwise stated.

Analytical Procedures. The hydrogen peroxide was titrated with potassium permanganate. The pH was measured with a combined glass−calomel electrode (Schott Geräte, type H6280) standardized with a phosphate buffer (pH 7.12 at 0 °C) and with a saturated solution of calcium hydroxide (pH 13.4 at 0 °C).[25] The temperature was kept constant in the range ±1 °C, and the pH was fixed within 0.1 unit. The pH values were uncorrected for the solutions used in NMR which contained 20% D_2O.

Results

(1) Influence of the Hydrogen Peroxide Concentration. Concentrated (1 M) solutions of sodium molybdate were used in order to get ^{95}Mo NMR data on a relatively short time scale (about 5 min). The temperature was kept at 0 °C to minimize changes during the recording of the spectra. Kinetics, ^{95}Mo NMR, spectra and UV spectroscopic measurements were realized under similar conditions (pH, temperature, and molybdate concentration) in order to make the comparison of the results obtained by these different techniques more reliable.

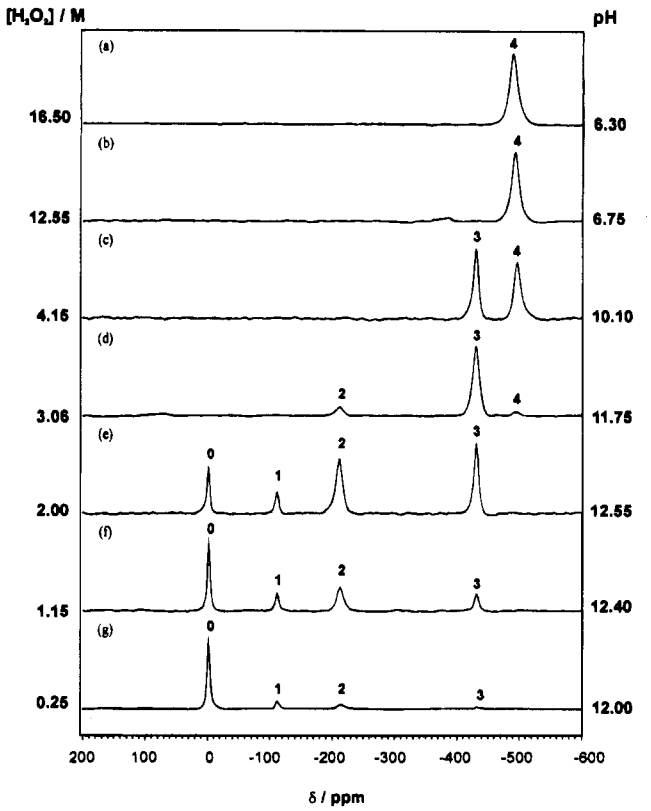

Figure 1. ^{95}Mo NMR spectra for (b−g) different H_2O_2 concentrations (0 °C, natural pH, $[Na_2MoO_4]$ = 1 M) and (a) tetraperoxomolybdate $Na_2Mo(O_2)_4\cdot 4H_2O$ (1 M) dissolved into H_2O_2 (12.5 M).

^{95}Mo NMR. Spectra of the known peroxomolybdates at natural pH were recorded: (i) the tetraperoxomolybdate $Na_2Mo(O_2)_4\cdot 4H_2O$ (1 M) dissolved into 12.5 M hydrogen peroxide (spectrum a) and (ii) the tetraperoxodimolybdate $K_2[Mo_2O_3(O_2)_4]\cdot 4H_2O$ (0.1 M) dissolved in pure water. Then, we investigated molar solutions of sodium molybdate with increasing concentrations of hydrogen peroxide (Figure 1). The NMR spectra feature five narrow peaks (**0**−**4**) which appear successively at decreasing chemical shifts as the hydrogen peroxide concentration increases (compound **4** has the most shielded ^{95}Mo nucleus).

UV/Visible Spectrophotometry. The molar solution of sodium molybdate is initially colorless. It becomes successively yellow, orange, and red-brown when the concentration of the hydrogen peroxide increases. The absorption spectra of the solutions previously analyzed by ^{95}Mo NMR were recorded without dilution between 200 and 900 nm. For these high concentrations, the signal is saturated in the spectral range below 700 nm. Therefore, the absorbance was measured in the decreasing part of the spectrum at 715 nm (Figure 2).

At this wavelength, the absorbance is essentially due to the tetraperoxomolybdate (ϵ = 440 ± 34 $M^{-1}\cdot cm^{-1}$ at 450 nm[12]). Its molar extinction coefficient at 715 nm (ϵ = 2.2 ± 0.1 $M^{-1}\cdot cm^{-1}$) was measured by dissolving 1 M of this crystallized compound into H_2O_2 (15 M). It is noteworthy that the absorbance at 715 nm falls to zero when the concentration of the hydrogen peroxide is smaller than 2 M. Then, it becomes significant between 2 and 3 M, and finally, it notably increases from 3.5 to 8 M.

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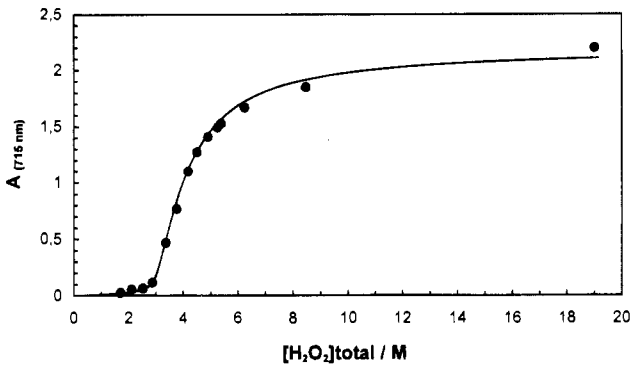

Figure 2. Influence of the concentration of hydrogen peroxide on the absorbance of a molar sodium molybdate solution at 715 nm (0 °C, natural pH): Dots, experimental values; line, curve calculated from eq 8.

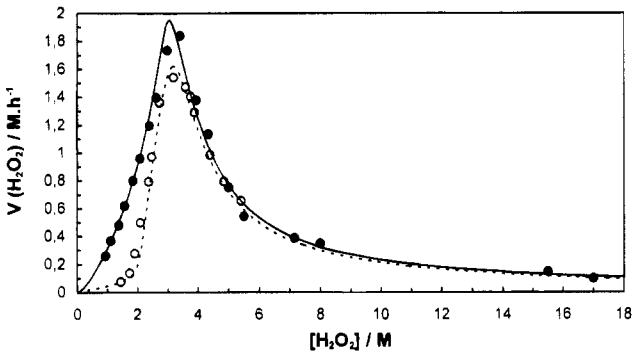

Figure 3. Disproportionation rate of H_2O_2 vs its concentration (0 °C, $[Na_2MoO_4]$ = 1 M). Experiments were carried out at natural pH (●) and at pH 10 (○). The curves were calculated from the equilibrium and rate constants given in the text.

Kinetics of the Disproportionation of H_2O_2 by Molybdate Ions. A hydrogen peroxide solution at natural pH and 0 °C was allowed to decompose in the presence of molybdate ions (1 M). The disappearance of H_2O_2 was monitored by titration with potassium permanganate, and the disproportionation rate of the hydrogen peroxide ($d[H_2O_2]/dt$) was calculated (Figure 3). In order to check that rate variations were not simply due to pH changes, we performed the same experiment while keeping the pH of the reaction medium to a constant value of 10 (Figure 3). However, we could not study the kinetics of the disproportionation of the hydrogen peroxide for concentrations in H_2O_2 exceeding 6 M at pH 10. The huge amount of sodium hydroxide necessary to keep constant the pH induced a significant "spontaneous" disproportionation of H_2O_2 even when reactants of the purest chemical grade were used.

The rates reported in Figure 3 were obtained from one solution, the decomposition of which was followed during several hours. Hence, they correspond to a steady state and could differ from the initial rates of H_2O_2 disproportionation. For the highest concentrations of hydrogen peroxide, we replaced the molybdate by crystallized tetraperoxomolybdate dissolved in 15 M hydrogen peroxide.

Both sets of experimental dots exhibit a bell-shaped arrangement and present a well-defined maximum for a hydrogen peroxide concentration of 3 M. At pH 10, the maximum is equal to 1.55×10^{-2} M·h^{-1} whereas, at natural pH, it reaches the value of 1.85×10^{-2} M·h^{-1}. The rates are also different for each pH when the hydrogen peroxide concentrations are lower than 3 M whereas, for higher concentrations, the kinetics of the disproportionation of H_2O_2 are similar at natural pH and at pH 10.

(2) Influence of the pH at Different H_2O_2/Mo Molar Ratios. (a) H_2O_2/Mo = 1. The main peak corresponds to the molybdate whatever the pH is. Nevertheless, these conditions are the most favorable for the appearance of peak **1**, the amount of which never exceeds 15% whatever the H_2O_2/Mo ratios are. The spectra obtained at different pH values do not show any significant change in the chemical shift of this peak **1** (δ = −110 ppm).

(b) H_2O_2/Mo = 2. When sodium molybdate (1 M) is added to hydrogen peroxide (2 M), the medium becomes very alkaline (pH = 12.2) and the ^{95}Mo NMR spectrum presents four narrow peaks noted **0**−**3**. By addition of 0.2 equiv of concentrated hydrochloric acid, we observe a slight upfield shift of peak **2** and the appearance of a broad peak (**2a**) at −285 ppm. As the pH decreases further, peak **2** progressively gets closer to peak **2a**. From about pH 10 to 6.9, only the very broad peak at −285 ppm is observed. On the contrary, the chemical shifts of the peaks **1** and **3** are left almost unchanged in the pH range 12.2−10.1. At lower pH, these peaks progressively disapppear as peak **2a** is increasing. At pH 2.6, we do not observe any peak under the usual conditions but an acquisition of the NMR signal overnight allows to detect a single broad peak at −270 ppm. Moreover, the NMR spectrum of an aqueous solution (0.1 M) of yellow crystals of the tetraperoxodimolybdate $K_2[Mo_2O_3(O_2)_4]\cdot 4H_2O$ consists of a broad signal at about the same chemical shift (−270 ppm).

(c) H_2O_2/Mo = 3.5. From pH 10.9 to 7.8, only peaks **3** and **4** are observed. The chemical shift of peak **4** does not depend upon pH (δ = −496 ppm). Peak **3**, however, experiences a downfield shift and a progressive broadening with decreasing pH (Table 1).

Table 1. Chemical Shifts of Peak **3** as a Function of pH (0 °C; $[H_2O_2]$ = 3.5 M; $[Na_2MoO_4]$ = 1 M)

HCl equiv	pH	chem shifts δ (ppm)	half-width $\Delta\nu_{1/2}$ (Hz)
0.000	10.90	−435	190
0.250	9.15	−429	200
0.350	8.50	−422	270
0.425	8.15	−409	360
0.500	7.90	−396	470
0.625	7.50	−368	500

From pH 7.8 to 5.5, peaks **3** and **4** progressively disappear. The above mentioned broad peak **2a** (δ = −285 ppm) is observed again from lower pH. An overnight spectrum at pH 5.1 reveals a second less intense peak at −208 ppm (peak **3a**).

Le Carpentier et al. have determined the crystal structure of a pyridinium salt of a peroxomolybdate with the ratio peroxo/Mo = 3, the dipyridinium bis(μ-hydroperoxo)tetraperoxodioxodimolybdate(VI) $[Hpy]_2[MoO(O_2)_2OOH]_2$.[26,27] It is obtained after crystallization, in H_2O_2 (10 M), of another peroxomolybdate, the dipyridinium (μ-oxo)tetraperoxodioxodiaquodimolybdate(VI) $[Hpy]_2[Mo_2O_3(O_2)_4(H_2O)_2]$, with a ratio peroxo/Mo = 2. In order to determine the chemical shift corresponding to the first peroxoanion $[MoO(O_2)_2OOH]_2^{2-}$, the ^{95}Mo NMR spectrum of a solution of the second peroxomolybdate in H_2O_2 (10 M) was recorded. After a prolonged acquisition (48 h), we observed a peak at −200 ppm (peak **3a**).

(d) H_2O_2/Mo = 15.5. Solid tetraperoxomolybdate was dissolved into concentrated hydrogen peroxide (15.5 M), and increasing amounts of concentrated hydrochloric acid were added. Between pH 10 and 5, we always observe a single

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narrow peak **4** ($\delta = -496$ ppm, $\Delta\nu_{1/2} = 250$ Hz). For lower pH, the solution, initially brownish-red, becomes yellow and a broad peak (peak **3a**, $\delta = -200$ ppm, $\Delta\nu_{1/2} = 700$ Hz) replaces peak **4**.

(3) Evolution of the Species in Very Alkaline Media for a Molar Ratio H_2O_2/Mo = 5. In very alkaline medium (pH = 14), the decomposition rate of hydrogen peroxide strongly decreases and the solution becomes colorless. We recorded ^{95}Mo NMR spectra for lower concentrations of hydrogen peroxide and of sodium molybdate (respectively 0.5 and 0.1 M) in order to reach very high pH and to bleach the solution by addition of sodium hydroxide. At pH 14, the solution is colorless and the corresponding spectrum is identical to the one obtained with low ratios H_2O_2/Mo (see above). As small aliquots of HCl were added to it, the solution became slightly colored again turning from pale yellow to brownish-red. Peaks **2**, **3**, and then **4** successively reappear.

Discussion

Crystallized Peroxomolybdates. Several reports deals with the formation of mono-, di-, or polynuclear complexes of molybdenum(VI) during the reaction between hydrogen peroxide and molybdate ions at different pH. In these complexes, the metal atom is surrounded by 1, 2, 3, or 4 peroxo ligands and one or two protons may be gained by acidification of the medium. Some complexes have been isolated as monocrystals and led to a thorough structural study by X-ray diffraction, but most of the other peroxomolybdates have been characterized less accurately by techniques such as UV/visible, IR, and Raman spectroscopies.[10-16,21,26-31]

The existence of a monoperoxide $MoO_3(O_2)^{2-}$ has never been directly proven. On the other hand, the formation of various diperoxomolybdates such as $Mo_2O_3(O_2)_4^{2-}$ and $MoO(O_2)_2L_2$ is well-established by X-ray diffraction.[11,13,15,17-20,32] The existence of a triperoxomolybdate $MoO(O_2)_3^{2-}$ in solution has been suggested in particular by Csanyi, but no well-defined mononuclear compound has ever been analyzed by X-ray diffraction.[12,14] On the other hand, Le Carpentier et al.[26,27] have established the structure of a dinuclear pyridinium salt $[MoO(O_2)_2OOH]_2^{2-}$, **7**, which corresponds to a dimer of the monoprotonated triperoxomolybdate $HMoO(O_2)_3^-$. The tetraperoxomolybdate $Mo(O_2)_4^{2-}$, **8**, is the most peroxidized species. It is a red-brown unstable complex, obtained by reaction of concentrated hydrogen peroxide with a neutral or alkaline solution of molybdate ions. Its structure has been established by X-ray diffraction and Raman spectroscopy[16] and is related to the one of the molybdate ion.

We have recorded the ^{95}Mo NMR spectra of the peroxomolybdates **7** and **8** by dissolving these crystallized compounds under conditions of pH and concentration of hydrogen peroxide suitable for their formation. The resulting data are reported in Table 2. The comparison of these results with the spectra recorded for the $MoO_4^{2-}/H_2O_2/H^+$ system allows us to assign some of the observed peaks.

The broad peak **2a** corresponds to the tetraperoxodimolybdate $Mo_2O_3(O_2)_4^{2-}$. Actually, the NMR spectrum of a 0.1 M solution of an authentic sample of $K_2[Mo_2O_3(O_2)_4].4H_2O$, **5**, at natural pH (5.5) mainly shows a broad peak at -270 ppm. Its chemical shift depends upon changes in the pH. Campbell et al.[21] did the same observations and also assigned this peak to $Mo_2O_3(O_2)_4^{2-}$. On the other hand, when sodium hydroxide was added to the solution of tetraperoxodimolybdate (pH 9.8), peaks **0**, **1**, and **3** appeared. Peak **3a** ($\delta = -200$ ppm, $\Delta\nu_{1/2} \approx 700$ Hz) obtained by dissolving $[Hpy]_2[Mo_2O_3(O_2)_4(H_2O)_2]$ into H_2O_2 (10 M) can be assigned, on the basis of the results obtained by Beiles[33] and Le Carpentier,[26,27] to the dimeric triperoxide species $[MoO(O_2)_2OOH]_2^{2-}$, **7**. The peak **4** (-496 ppm), relatively narrow ($\Delta\nu_{1/2} \approx 250$ Hz), is unambiguously assigned to the tetraperoxomolybdate $Mo(O_2)_4^{2-}$, **8**, the most peroxidized species. It is the only peak observed at very high concentration of hydrogen peroxide in neutral and alkaline medium, and it is also obtained by dissolving into H_2O_2 (12.5 M) the tetraperoxomolybdate previously prepared according to reported procedures (spectrum a).

Table 2. ^{95}Mo NMR Data, Experimental Conditions, and Assignment for the Different Peaks Observed at 0 °C with the $MoO_4^{2-}/H_2O_2/H^+$ System

peak no.	δ (ppm)	$\Delta\nu_{1/2}$ (Hz)	H_2O_2/Mo	pH range	assgnts
0	0	100	0–3	7–14	MoO_4^{2-}
1	−110	130	0–3	7–14	$MoO_3(O_2)^{2-}$
2a	−265 to −285[a,b]	900[c]	0–3.5	2–12	$Mo_2O_3(O_2)_4^{2-}$
2	−215 to −230[b]	250	0–3	10–13.5	$MoO_2(O_2)_2^{2-}$
3a	−200	700	>3	2.5–5.5	$[MoO(O_2)_2OOH]_2^{2-}$
3	−368 to −435[b]	190–500[b]	0–10	7–13.5	$MoO(O_2)_3^{2-}$
4	−496	250	>3	5–12	$Mo(O_2)_4^{2-}$

[a] Uncertainty due to the excessive broadness of the peak. [b] Influence of the pH value (e.g. see Table 1). [c] Approximative value to the different recording and computing parameters.

Table 3. ^{95}Mo NMR Data and Assignments Reported by Campbell et Al.[21] (H_2O_2/Mo = 5/1, T = 25°C)

pH	chem shifts (ppm)	assgnts
8.2–8.0	−426.5	$Mo(O_2)_4^{2-}$
	−496.0	$MoO(O_2)_3^{2-}$ or $MoO(O_2)_3(H_2O)^{2-}$
7.2–5.0	−492.3	$MoO(O_2)_3^{2-}$ or $MoO(O_2)_3(H_2O)^{2-}$
	−266	$Mo_2O_3(O_2)_4(H_2O)^{2-}$
5.0–2.5	−263	$Mo_2O_3(O_2)_4(H_2O)^{2-}$

Peroxomolybdates in Solution with Various Concentrations of Hydrogen Peroxide. When the ^{95}Mo NMR spectra were recorded at natural pH with various hydrogen peroxide concentrations (Figure 1), four narrow peaks **1**–**4** are observed (Table 2), besides the peak **0** (MoO_4^{2-}). The assignments of peaks **1**–**3** are less straightforward than for peak **4**. An increase of the hydrogen peroxide concentration gradually leads to the appearance of signals with chemical shifts moving toward higher fields. Moreover, peaks **2** and **3** are the major peaks respectively for 2 and 3 M hydrogen peroxide when $[Na_2MoO_4] = 1$ M, as they are for 0.2 and 0.3 M hydrogen peroxide when $[Na_2MoO_4] = 0.1$ M. In each case, the H_2O_2/Mo ratios are respectively 2 and 3. Hence peaks **1**–**3** could be assigned to peroxo complexes with an increasing number of peroxo bridges, i.e. the monoperoxomolybdate $MoO_3(O_2)^{2-}$ ($\delta = -110$ ppm, $\Delta\nu_{1/2} \approx 130$ Hz), the diperoxomolybdate $MoO_2(O_2)_2^{2-}$ ($\delta = -215$ ppm, $\Delta\nu_{1/2} \approx 250$ Hz), and the triperoxomolybdate $MoO(O_2)_3^{2-}$ ($\delta = -435$ ppm, $\Delta\nu_{1/2} \approx 190$ Hz). These compounds result from a simple exchange of the oxo ligands present in MoO_4^{2-} by peroxo ligands and give dianionic complexes with the general molecular formula $Mo(O_2)_nO_{4-n}^{2-}$. Campbell et al.[21] have also reported, some years ago, ^{95}Mo NMR data about the different peroxomolybdates formed in aqueous solution (pH < 8.8). Some of their results are summarized in Table 3.

Our experimental results are essentially in a good agreement with these reported data. Nevertheless, our interpretation

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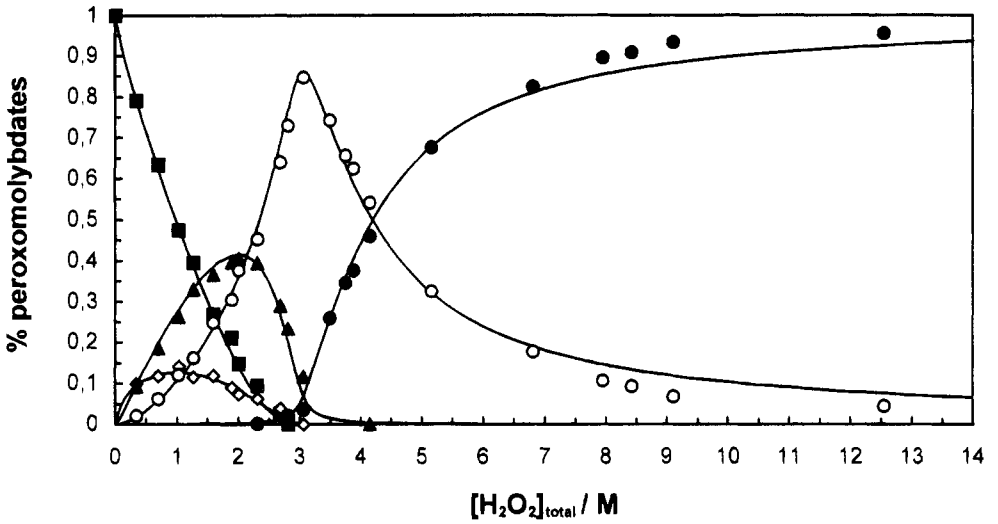

Figure 4. Relative area (in %) for peaks **0**−**4** as a function of the total concentration of hydrogen peroxide (0 °C, natural pH, $[Na_2MoO_4] = 1$ M). Dots: experimental data; MoO_4^{2-}, ■; peak **1**, ◇; peak **2**, ▲; peak **3**, ○; peak **4**, ●. Solid lines: curves calculated from the equilibria (2)−(5).

concerning both peaks at −426 and −496 ppm is quite opposite. It is supported by the following:

Campbell et al. reported a time dependence of the relative intensities of these peaks. They observed that the peak at −496 ppm increased at the expense of peak at −426 ppm in such a manner that each one should correspond to products which are related through an equilibrium. Figure 1 clearly shows, however, that, for decreasing H_2O_2 concentrations, the peak at −496 ppm disappears before the peak at −426 ppm.

Moreover, they did not mention the peak at −426 ppm when $H_2O_2/Mo = 2$ whereas Figure 1 shows that peak **3** is already present for this ratio and that peak **4** only appears for higher molar ratios. One should notice however that the pH of the solutions prepared by Campbell et al. never exceeded 8.8 and that we, too, did not observe peak **3** below this pH.

We have reported in Figure 4 the evolution of the concentration of the species related to each peak (from peak **0** to peak **4**) as a function of the total concentration of hydrogen peroxide. The relative percentages for each species were estimated from the area (uncertainty ±10%) of the peaks for different H_2O_2 concentrations. Under our experimental conditions, the rate of decomposition of H_2O_2 is relatively slow (<0.04 M·min^{-1}) and we can consider that the equilibria (2)−(5) are established between the peroxomolybdates and free hydrogen peroxide.

$$MoO_4^{2-} + H_2O_2 \rightleftharpoons MoO_3(O_2)^{2-} + H_2O \qquad K_1 = 1.5 \times 10^2 \tag{2}$$

$$MoO_3(O_2)^{2-} + H_2O_2 \rightleftharpoons MoO_2(O_2)_2^{2-} + H_2O \qquad K_2 = 1.2 \times 10^3 \tag{3}$$

$$MoO_2(O_2)_2^{2-} + H_2O_2 \rightleftharpoons MoO(O_2)_3^{2-} + H_2O \qquad K_3 = 2.1 \times 10^2 \tag{4}$$

$$MoO(O_2)_3^{2-} + H_2O_2 \rightleftharpoons Mo(O_2)_4^{2-} + H_2O \qquad K_4 = 1.4 \pm 0.1 \tag{5}$$

Since the concentration of free hydrogen peroxide cannot be measured, the values of the constants K_1, K_2, and K_3 cannot be directly calculated. On the other hand, the ratios K_n/K_{n-1} of two successive constants can be expressed as a function of the sole peroxomolybdate concentrations (eq 6). Thus, replacing these concentrations by the area of the corresponding ^{95}Mo NMR peaks led us to evaluate these ratios, where n is the number of peroxo groups bound to molybdenum ($n \geq 2$).

$$\frac{K_n}{K_{n-1}} = \frac{[MoO_{4-n}(O_2)_n^{2-}][MoO_{6-n}(O_2)_{n-2}^{2-}]}{[MoO_{5-n}(O_2)_{n-1}^{2-}]^2} \tag{6}$$

However, for high concentrations of hydrogen peroxide (>3.5 M), the amount of free H_2O_2 becomes significant and can be calculated. Thus, from the relative area of the ^{95}Mo NMR peaks of the tri- and the tetraperoxo molybdates, $K_4 = [Mo(O_2)_4^{2-}]/[MoO(O_2)_3^{2-}] \times [H_2O_2]_{free}$ was determined for 3.5 M < $[H_2O_2]_{tot.}$ < 5 M, which corresponds to the conditions under which both peroxomolybdates are in sufficient amounts. The average value of K_4 was estimated to 1.4. On the other hand, K_4 was determined more easily by UV/visible spectroscopy as $Mo(O_2)_4^{2-}$ exhibits also a characteristic spectral band. A linear relationship between the absorbance at 715 nm of the tetraperoxomolybdate and the hydrogen peroxide concentration was established according to eq 7, where $A_{tetra} = 2.20$ and $A_{tri} =$ 0.07 are respectively the higher values of the absorbance of the tetra- and the triperoxomolybdates at 715 nm and n represents the number of H_2O_2 molecules exchanged.

$$\log \frac{A - A_{tri}}{A_{tetra} - A} = \log K_4 + n \log [H_2O_2]_{free} \tag{7}$$

When eq 7 is applied to the experimental results shown in Figure 2, a linear variation is obtained. The calculated slope is 0.996, and the intercept is 0.120 leading to $K_4 = 1.32$. The first value confirms the participation of only one H_2O_2 molecule to the equilibrium, and the second one is in fair agreement with the equilibrium constant found by ^{95}Mo NMR. The curve plotted in Figure 2 was calculated (eq 8) from the values of the different equilibrium constants given above. The molar extinction coefficient at 715 nm for triperoxomolybdate was estimated to 0.07 ± 0.01 M^{-1}·cm^{-1}. It accounts for the faint absorbance between 2 and 3 M.

$$A_{(715\ nm)} = 0.07[MoO(O_2)_3^{2-}] + 2.2[Mo(O_2)_4^{2-}] \tag{8}$$

In the same way, the curves representing the evolution of each species according to the hydrogen peroxide concentration can be plotted (Figure 4). Surprisingly, the fit of the experimental dots with these calculated curves is excellent although the determination of the peroxomolybdate concentrations from peak area is rather rough and the ionic strength of the solutions is not kept constant. Nevertheless, a slight discrepancy exists for high hydrogen peroxide concentrations ($[H_2O_2] > 8$ M). When the amount of H_2O_2 increases, the medium becomes more and more acidic (e.g. $[H_2O_2] = 12.5$ M, pH $\approx$ 6.5). The peroxomolybdates $MoO(O_2)_3^{2-}$ and $Mo(O_2)_4^{2-}$ can no more be considered as the sole species present in solution. The triperoxomolybdate $MoO(O_2)_3^{2-}$ has tendency to protonate giving $Mo_2O_3(O_2)_4^{2-}$ (eq 16) which corresponds to a broad peak, difficult to detect when it is present in small proportion. Thus, the experimental amounts of tri- and tetraperoxo molybdates cannot be described accurately from the simple scheme depicted in eqs 2–5.

Csanyi has carried out a study of the different equilibria which could occur at room temperature in dilute alkaline media.[12,29] He suggested the formation of four different peroxomolybdates related to the equilibria (9)–(11).

$$MoO_4^{2-} + 2H_2O_2 \rightleftharpoons HMoO_2(O_2)_2^- + H_2O + OH^- \qquad K_{2:2} = 2.44 \times 10^{-1} \qquad (9)$$

$$HMoO_2(O_2)_2^- + H_2O_2 + OH^- \rightleftharpoons MoO(O_2)_3^{2-} + 2H_2O \qquad K_{3:1} = 1.26 \times 10^{-8} \qquad (10)$$

$$MoO(O_2)_3^{2-} + H_2O_2 \rightleftharpoons Mo(O_2)_4^{2-} + H_2O \qquad K_{4:1} = 1.58 \qquad (11)$$

According to his view, the protonated form, $HMoO_2(O_2)^{2-}$, should be involved rather than the dianion, $MoO_2(O_2)_2^{2-}$, even in very alkaline media. We rather follow the representation proposed by Aubry[6] in which equilibrium 9 is splitted into a ligand exchange reaction (eq 12) and a protonation reaction of

$$MoO_4^{2-} + 2H_2O_2 \rightleftharpoons MoO_2(O_2)_2^{2-} + 2H_2O \qquad (12)$$

$$MoO_2(O_2)_2^{2-} + H_3O^+ \rightleftharpoons HMoO_2(O_2)_2^- + H_2O \qquad K_a = 7.9 \times 10^{-10} \qquad (13)$$

the resulting $MoO_2(O_2)_2^{2-}$ (eq 13). Furthermore, considering the high molybdate concentrations used in our study, we have to take into account the dimerization of $HMoO_2(O_2)_2^-$ into $Mo_2O_3(O_2)_4^{2-}$. Moreover, the acid–base equilibrium of hydrogen peroxide must be considered (eq 14).[34]

$$H_2O_2 + H_2O \rightleftharpoons HOO^- + H_3O^+ \qquad K_{a'} = 2.51 \times 10^{-12} \qquad (14)$$

The equilibrium constants given by Csanyi differ from ours, except for the equilibrium between tri- and tetraperoxomolybdates. The experimental conditions required to record the NMR spectra of unstable peroxomolybdates (i.e. concentrated sodium molybdate (1 M) and low temperature (0 °C)) were, however, quite different from those used by Csanyi (dilute sodium molybdate (10^{-3} M) and room temperature). Moreover, the determination of the equilibrium constants between the mono-, di- and triperoxomolybdates by UV/visible spectroscopy should be less reliable as these species exhibit very close UV absorption bands whereas tetraperoxomolybdate shows a characteristic absorption band around 450 nm.

pH Influence. *H_2O_2/Mo = 2. This study reveals the presence of two diperoxomolybdic compounds. The first one, obtained alone when pH > 12, appears as a narrow peak (peak **2**). The second one, obtained alone when pH < 9, is characterized by a very broad peak (peak **2a**) (see Table 2). When 9 < pH < 12, both peaks are observed.

Because of the low molybdate concentration (10^{-3} M), only mononuclear species are implicated in the equilibria (9)–(11). This must still be the case in very alkaline and highly concentrated media, as the sharpness of peaks **1**–**4** supports it. On the other hand, polycondensation is favored in acidic media. Thus, it seems very likely that the protonated diperoxoanion $HMoO_2(O_2)_2^-$ mainly exists as a dimer or even more as a polymer and the equilibrium (13) must be replaced by (15).

$$2MoO_2(O_2)_2^{2-} + 2H_3O^+ \rightleftharpoons Mo_2O_3(O_2)_4^{2-} + 3H_2O \qquad (15)$$

Monoprotonation of the diperoxomolybdate $MoO_2(O_2)_2^{2-}$ consists in a rapid exchange (eq 17) on the ^{95}Mo NMR time scale. Therefore, only one peak **2** showing a pH dependence is observed for both species $MoO_2(O_2)_2^{2-}$ and $HMoO_2(O_2)_2^-$. Actually, when the acidity of the medium increases, peak **2** shifts slightly upfield. On the other hand, the dimerization equilibrium of $HMoO_2(O_2)_2^-$ into $Mo_2O_3(O_2)_4^{2-}$ is probably slow when compared to the acquisition time of the NMR signal and a distinct broad peak (**2a**) appears on the spectra. Hence, this second peak would rather correspond to the dimeric species $Mo_2O_3(O_2)_4^{2-}$ or to even more condensed diperoxomolybdates. In agreement with this view, a similar peak is obtained from an aqueous solution of solid $K_2Mo_2O_3(O_2)_4{\cdot}4H_2O$. The value of the apparent pK_a related to the equilibrium (15) was estimated to 10.8 according to ^{95}Mo NMR. It clearly differs from the one found for the equilibrium $HMoO_2(O_2)_2^-/MoO_2(O_2)_2^{2-}$ in diluted solutions (pK_a = 9.1). This discrepancy further supports the involvement of a dimerization of $MoO_2(O_2)_2^{2-}$ into $Mo_2O_3(O_2)_4^{2-}$ at high concentrations.

***H_2O_2/Mo = 3.5.** From pH 12 to 7.8, we can observe a progressive shift toward the low field of peak **3** (Table 1). This phenomenon suggests a protonation of $MoO(O_2)_3^{2-}$.[35] When pH $\leq$ 7.5, the broad peak corresponding to $Mo_2O_3(O_2)_4^{2-}$ (δ = −270 ppm) is observed again. Thus the following equilibrium between $MoO(O_2)_3^{2-}$ and $Mo_2O_3(O_2)_4^{2-}$ takes place (eq 16).

$$2MoO(O_2)_3^{2-} + 2H_3O^+ \rightleftharpoons Mo_2O_3(O_2)_4^{2-} + 2H_2O_2 + H_2O \qquad (16)$$

On the other hand, the chemical shifts of peaks **1** and **4** are left almost unchanged at any pH. Therefore, the corresponding protonated species such as $HMoO_3(O_2)^-$, $H_2MoO_3(O_2)$, $HMo(O_2)_4^-$, and $H_2Mo(O_2)_4$[10,12,14,36,37] have not been observed.

***H_2O_2/Mo = 15.5.** There is no tetraperoxomolybdate (peak **4**) left when pH $\approx$ 5; the red-brown solution becomes yellow, and a broad peak **3a** (δ = −200 ppm) replaces peak **4**. This broad peak, also obtained below pH 5 as a minor species for H_2O_2/Mo = 3.5, is assigned to the dimeric species of triperoxomolybdate, $[MoO(O_2)_2OOH]_2^{2-}$, **7**, by comparison with the

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spectrum of an authentic sample of the latter species. Tetraperoxomolybdate would be converted into a condensed acidic form of triperoxomolybdate when the pH of the solution decreases (eq 17).

$$2Mo(O_2)_4^{2-} + 2H_3O^+ \rightleftharpoons [MoO(O_2)_2OOH]_2^{2-} + 2H_2O_2 \quad (17)$$

* Alkaline Media

Under such conditions, H_2O_2 mainly exists as its deprotonated form HOO^- (pH > pK_a). Thus, the different peroxomolybdates undergo hydrolysis according to equilibrium 18. The ^{95}Mo NMR

$$MoO_{4-n}(O_2)_n^{2-} + nOH^- \rightleftharpoons MoO_4^{2-} + nHOO^- \quad (18)$$

spectrum of a very alkaline colorless solution (pH = 14) containing $[Na_2MoO_4] = 0.1$ M and $[H_2O_2] = 0.5$ M exhibits essentially the molybdate (peak **0**), along with a weak signal (peak **1**) corresponding to the monoperoxomolybdate. The spectra of the same solution recorded at lower pH values show the successive appearance of peaks **2**–**4**.

Kinetics of Hydrogen Peroxide Disproportionation. The rates of the decomposition of concentrated hydrogen peroxide solutions in the presence of sodium molybdate (1 M), at natural pH or at pH 10, present a well-defined maximum when the hydrogen peroxide concentration is equal to 3 M (Figure 3). This results suggests heavily that the triperoxomolybdate species should be the main precursor of molecular oxygen. Kinetic studies performed at pH 10 with 0.1 M sodium molybdate also agree with this view as the maximum rate is observed when hydrogen peroxide concentration is equal to 0.3 M. Furthermore, ^{95}Mo NMR has also revealed that peak **3**, corresponding to $MoO(O_2)_3^{2-}$, is the main signal when $[H_2O_2] = 3$ M at natural pH as well as at pH 10 (Figure 1).

For hydrogen peroxide concentrations >3 M, the triperoxomolybdate is converted into the tetraperoxomolybdate and the rate strongly decreases. In order to determine the decomposition rate of the tetraperoxomolybdate $Mo(O_2)_4^{2-}$, a crystallized sample of this compound was dissolved into concentrated hydrogen peroxide (15 M). Under these conditions, the solution still undergoes a decomposition but the reaction is about 20 times slower than the maximum value (Figure 3). However, by taking into account the equilibrium (5), we assess that about 2–5% of triperoxomolybdate is still present in solution in spite of the high hydrogen peroxide concentration. This low triperoxomolybdate concentration is sufficient to account for the measured decomposition rate. Thus, we may conclude that, even if the tetraperoxomolybdate can undergo a decomposition, its rate is very low compared with the one of the triperoxomolybdate and, in any case, lower than 0.1 $M^{-1}\cdot h^{-1}$.

If we compare the rate curves obtained at pH 10 and at natural pH, they differ only when the hydrogen peroxide concentration is <3 M. Actually, for $[H_2O_2] > 3$ M, the ^{95}Mo NMR study performed at pH 10 shows that only the tri- and the tetraperoxomolybdates are present in the solution. The relative amounts at pH 10 differ from less than 5% for a given hydrogen peroxide concentration from those obtained at natural pH. This concordance accounts for the similarity between the rates in this range of concentrations. On the contrary, for $[H_2O_2] < 3$ M, the NMR spectra at natural pH and at pH 10 are notably different for peak **2**. At natural pH, the medium is strongly alkaline (pH > 12) and the main peroxidized species is $MoO_2(O_2)_2^{2-}$. At pH 10, a part of $MoO_2(O_2)_2^{2-}$ is present as the dimer $Mo_2O_3(O_2)_4^{2-}$, which is stable in solution. Thus, the calculated rates for $[H_2O_2]$ < 3 M at pH 10 are lower than those obtained at natural pH for identical hydrogen peroxide concentrations.

The experimental rate constants may be calculated by using a theoretical model which supposes that the formation of singlet oxygen arises from an unimolecular decomposition of one or several peroxomolybdates (eq 19).

$$d[H_2O_2]/dt = k_1[MoO_3(O_2)^{2-}] + k_2[MoO_2(O_2)_2^{2-}] + k_3[MoO(O_2)_3^{2-}] + k_4[Mo(O_2)_4^{2-}] \quad (19)$$

The best fit is obtained by taking the values $k_1 = 0$, $k_2 = 0.2 \pm 0.1$, $k_3 = 2.2 \pm 0.1$, and $k_4 = 0$ h^{-1} for the individual rate constants of the decomposition of the mono-, di-, tri-, and tetraperoxomolybdates. It means that the formation of oxygen essentially occurs through the intermediary of the triperoxomolybdate, $MoO(O_2)_3^{2-}$ (eq 20).

$$MoO(O_2)_3^{2-} \xrightarrow{k_3} MoO_3(O_2)^{2-} + {}^1O_2 \quad (20)$$

It is noteworthy that the kinetic results reported here are equally consistent with a bimolecular process involving free hydrogen peroxide and diperoxomolybdate (eq 21).

$$MoO_2(O_2)_2^{2-} + H_2O_2 \rightarrow MoO_3(O_2)^{2-} + {}^1O_2 + H_2O \quad (21)$$

This mechanism seems less likely because it assumes the formation of an activated complex with a molybdenum atom surrounded by three peroxo bridges. This complex would be similar to the triperoxomolybdate while being different and should be very unstable since it is not detected by ^{95}Mo NMR. Therefore, although this assumption cannot totally be ruled out, we prefer the simpler mechanism (eq 20) taking into account the unimolecular decomposition of triperoxomolybdate.

Our interpretation contrasts with all the preceding reports. Until now, the unimolecular decomposition of the diperoxomolybdate was thought to be the main pathway of oxygen generation (eq 22) during the catalytic disproportionation of H_2O_2 by MoO_4^{2-} as reported by Baxendale,[37] Brauer,[7] Foote,[8] and Aubry.[6]

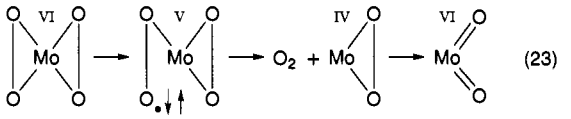
$$MoO_2(O_2)_2^{2-} \xrightarrow{k_2} MoO_4^{2-} + {}^1O_2 \quad (22)$$

Our kinetic study gives evidence for the involvement of the diperoxomolybdate, $MoO_2(O_2)_2^{2-}$, but it appears to be 10 times more stable than the triperoxomolybdate, $MoO(O_2)_3^{2-}$. This discrepancy arises from the difficulty met by the latter authors to determine accurately the concentration of $MoO(O_2)_3^{2-}$ in aqueous solution by UV spectroscopy. Actually, both complexes, $MoO_2(O_2)_2^{2-}$ and $MoO(O_2)_3^{2-}$, are generated simultaneously when H_2O_2 is added to MoO_4^{2-} solutions (Figure 1) and they exhibit very close UV spectra. On the contrary, ^{95}Mo NMR clearly distinguishes these compounds and leads to a good estimation of their concentrations which allows a straightforward correlation with kinetics.

On the other hand, Foote and Niu showed that an aqueous solution of the tetraperoxomolybdate in D_2O generates singlet oxygen when heated at 40 °C. They concluded that $Mo(O_2)_4^{2-}$ is a precursor of $^1O_2$.[8] By taking into account our results, this experiment may be re-interpreted by considering that when $Mo(O_2)_4^{2-}$ is dissolved into water, it is in part hydrolyzed into $MoO(O_2)_3^{2-}$ according to eq 5. Thus, the generation of $^1O_2$ is likely to occur from the decomposition of the triperoxomolybdate rather than from the much more stable tetraperoxomolybdate. Böhme and Brauer drew the same conclusion from their studies of $^1O_2$ IR chemiluminescence.[7] They observed that the

amount of $^1O_2$ decreased for higher H_2O_2 concentrations, and they concluded that the decomposition of $Mo(O_2)_4^{2-}$ does not significantly contribute to $^1O_2$ formation.

It has been shown that all the molecular oxygen generated through the catalyzed disproportionation of H_2O_2 by MoO_4^{2-} was in a singlet state, $^1O_2$ ($^1\Delta_g$).[6] The formation of this excited species from the triperoxomolybdate, $MoO(O_2)_3^{2-}$, can be rationalized in terms of spin conservation rule. Since the rate of H_2O_2 decomposition is first order with respect to the molybdate,[9,37] the formation of oxygen should occur through a redox reaction between two peroxo ligands bound to the same molybdenum atom. One possible mechanism (eq 23) involves

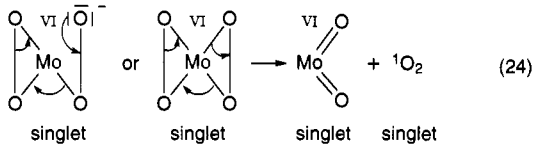


(23)

the central molybdenum(VI) atom, which would oxidize another one of the peroxo bridges into oxygen, and the resulting molybdenum(IV) would reduce another peroxo bridge into two oxo ligands giving back molybdenum(VI).

Such a mechanism has already been proposed in order to explain that bis(peroxo)molybdenum(VI) porphyrin complexes evolve singlet oxygen with concurrent formation of dioxo complexes both thermally[38] and photochemically.[39,40] Moreover, on the basis of extended Hückel calculations, Ledon et al. assume that the first step is an homolysis of a Mo−O bond affording formally a peroxosuperoxomolybdenum(V) complex.[41] This unstable intermediate would split off molecular oxygen providing a peroxomolybdenum(IV) complex which would give the dioxomolybdenum(VI) *via* an internal redox reaction. Nevertheless, if a homolytic cleavage of a Mo−O bond occurred, the primary singlet diradical should undergo, at least partially, an intersystem crossing leading to a triplet diradical which, through fragmentation, would produce some triplet oxygen.[42] This is contradictory to the experimental finding that 100% of the molecular oxygen evolved is in its singlet ($^1\Delta_g$) excited state: the reaction should proceed through a bi-electronic or a concerted pathway. On the other hand, the conversion of d^2 metal peroxides, such as peroxomolybdenum(IV) into d^0 *cis*-dioxo species such as dioxomolybdenum(VI), should be very unlikely on orbital symmetry considerations.[43,44]

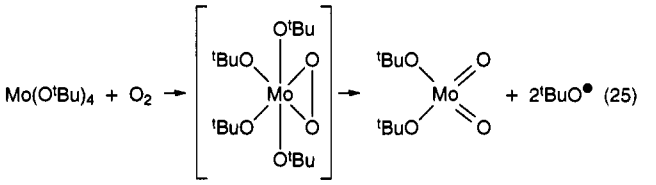
We rather think that this redox process directly occurs between two peroxo bridges without any change in the oxidation state of the molybdenum atom (eq 24) as no evidence supports



(24)

the involvement of molybdenum(IV). Moreover, we have shown that the disproportionation of hydrogen peroxide into singlet oxygen could also be catalyzed by metals such as calcium(II) which cannot change their oxidation state.[5]

A particular spectacular case of such simultaneous reduction of peroxide and oxidation of other ligands has been reported.[44-46] Dilute solutions of $Mo(O^tBu)_4$ react with oxygen to give $MoO_2(O^tBu)_2$ and *tert*-butoxy radicals (eq 25). The reaction appears to be unimolecular and takes place spontaneously without any change of the oxidation state of molybdenum during the cleavage step.



(25)

The quantitative formation of $^1O_2$ instead of $^3O_2$, which is energetically more feasible, can be accounted for by Wigner's rule which foresees that when a ground singlet state molecule suffers thermolysis into oxygen and a ground singlet state molecule, the total spin is kept unchanged. Thus, the generated oxygen should be in an excited singlet state.[47] This rule is valid for any concerted or ionic process as long as charge transfer occurs through bi-electronic process and without intersystem crossing (ISC). At the present time however, we cannot assert whether the decomposition of the triperoxomolybdate into singlet oxygen occurs through a concerted or an ionic pathway.

Conclusion

For the first time, by means of ^{95}Mo NMR spectroscopy, we have clearly established that four intermediates, i.e. $MoO_3(O_2)^{2-}$, $MoO_2(O_2)_2^{2-}$, $MoO(O_2)_3^{2-}$, and $Mo(O_2)_4^{2-}$, are formed during the disproportionation of H_2O_2 catalyzed by MoO_4^{2-} in alkaline media. By correlating these NMR results with kinetic data, we can now assert unambiguously that, among these intermediates, the main precursor of singlet oxygen is the triperoxomolybdate, $MoO(O_2)_3^{2-}$, and not the di- or the tetraperoxomolybdates, $MoO_2(O_2)_2^{2-}$ and $Mo(O_2)_4^{2-}$, which were thought until now to be the reactive species.

Supporting Information Available: ^{95}Mo NMR spectra for (i) $H_2O_2/Mo = 2$ at different pH values with the spectrum of $K_2[Mo_2O_3(O_2)_4]\cdot 4H_2O$ at pH 5.5, (ii) $H_2O_2/Mo = 3.5$ at different pH values with the spectrum of $[Hpy]_2[MoO(O_2)OOH]_2$ (0.05 M) at pH 2.60, and (iii) $H_2O_2/Mo = 5$ in very alkaline media and a figure showing the structures of **5** ($O[MoO(O_2)_2]_2^{2-}$), **6** ($MoO(O_2)L_2$), **7** ($[MoO(O_2)_2OOH]_2^{2-}$), and **8** ($Mo(O_2)_4^{2-}$) (5 pages). Ordering information is given on any current masthead page.

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