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Generation of Singlet Oxygen from Hydrogen Peroxide Disproportionation Catalyzed by Molybdate Ions

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Measurements of the infrared phosphorescence of singlet molecular oxygen ($^1O_2$) at 1270 nm have been used to demonstrate that $^1O_2$ is formed during the disproportionation of hydrogen peroxide catalyzed by molybdate ions. The results of measurements at hydrogen peroxide concentrations in the range $0.10 \leq [H_2O_2] \leq 0.30$ are consistent with the assumption that MoO_6^{2-} and MoO_8^{2-} are formed. However, the decomposition of MoO_8^{2-} does not significantly contribute to $^1O_2$ formation. For the reaction $MoO_6^{2-} \rightarrow MoO_4^{2-} + {}^1O_2$, the activation parameters $E_a = 15.6 \pm 1.2$ kcal·mol^{-1} and $\log A = 9.1 \pm 0.9$ have been evaluated.

Introduction

The disproportionation of hydrogen peroxide into water and singlet molecular oxygen in its $^1\Delta_g$ state ($^1O_2$)

$$2H_2O_2 \rightarrow 2H_2O + {}^1O_2 \qquad (1)$$

should occur spontaneously at room temperature, since this reaction is allowed on both thermodynamic and spin-conservation grounds.[1,2] However, it is well-known that reaction 1 is kinetically inhibited; its rate is extremely low at room temperature.[2]

Recently, Aubry reported that several inorganic compounds can catalyze reaction 1 in basic aqueous solutions.[3] In particular, the molybdate ion was found to be an efficient catalyst.[4–6] The evidence for the generation of $^1O_2$ via the catalyzed reaction 1 was obtained indirectly using various water-soluble $^1O_2$ acceptors as $^1O_2$ traps, e.g. tetrapotassium rubrene-2,3,8,9-tetracarboxylate (RTC),[3] which reacts with $^1O_2$ providing the corresponding endoperoxide ($RTCO_2$).

Chemical traps for $^1O_2$ (e.g. RTC) are unfortunately not unambigous in their effect. This was stringently demonstrated by Mulazzani et al. for the $^1O_2$ trap 9,10-anthracenedipropionate.[7] Chemical traps for $^1O_2$ suffer from several disadvantages which are discussed in detail in the paper of Aubry.[3] In addition it must be noted that endoperoxides of aromatic hydrocarbons have the important drawback that they are thermally labile. Thus the activation parameters of a thermal reaction producing $^1O_2$ cannot accurately be determined with aromatic hydrocarbons as $^1O_2$ traps.

In contrast, the infrared luminescence (IRL) at 1.27 μm resulting from the weak radiative transition of $^1O_2$ can be used as specific and unequivocal proof for $^1O_2$

$$O_2(^1\Delta_g) \xrightarrow{k_P} O_2(^3\Sigma_g^-) + h\nu \qquad (2)$$

The present work is concerned with studies of the disproportionation of H_2O_2 catalyzed by molybdate ions using the IRL method.

Experimental Section

Materials. H_2O was distilled twice. Stabilizer-free hydrogen peroxide (30%, Merck, Perhydrol Suprapur), sodium molybdate ($Na_2MoO_4{\cdot}2H_2O$, Puriss pa, Fluka), disodium hydrogen phosphate (Na_2HPO_4, Suprapur, Merck), trisodium phosphate ($Na_3PO_4{\cdot}12H_2O$, pa, Merck), potassium iodide (pa Merck), 0.1 M sodium thiosulfate solution (Fixanal, Riedel-de Haen), and ethylenediaminetetraacetic acid (EDTA, pa Merck) were used as purchased.

Singlet Oxygen Infrared Emission Measurements. The near-infrared detection system mostly used in our studies consisted of a chopper, 1.27-μm interference filter, liquid nitrogen cooled germanium diode and muon filter (North Coast, EO 817 L and 829B), lock-in amplifier, and recorder. Reactions were carried out in a 1-cm quartz cuvette placed directly in front of the chopper. The cuvette holder is connected with a thermostat. Our home-built IRL spectrometer, which can be modified to record also the phosphorescence spectrum of $^1O_2$, has been described in detail.[8,9]

The intensity of the $^1O_2$ phosphorescence emission, I_P, under steady-state conditions is given by the expression

$$I_P = ck_p[^1O_2]_s \qquad (I)$$

In this expression c is a constant of the IRL spectrometer and k_p is the rate constant of the phosphorescence emission. In water, a value of $k_p = 0.18$ s^{-1} was determined by Schmidt and Afshari.[10] In addition $[^1O_2]_s$ denotes the stationary concentration of $^1O_2$.

If only the phosphorescence emission (reaction 2) and the quenching by the solvent (reaction 3) are responsible for the deactivation of $^1O_2$,

$$^1O_2 \xrightarrow{k_\Delta} {}^3O_2 \qquad (3)$$

with $k_\Delta \gg k_P$, then $[^1O_2]_s$ is given by the following expression:

$$[^1O_2]_s = v_{^1O_2}\tau_\Delta \qquad (II)$$

where $v_{^1O_2}$ denotes the rate of $^1O_2$ formation and $\tau_\Delta = 1/k_\Delta$ represents the lifetime of $^1O_2$. From measurements of the phosphorescence emission of $^1O_2$ generated by electronically excited sensitizers (e.g. methylene blue), we have calculated that the lowest value of $[^1O_2]_s$, which can be measured with our very sensitive IRL spectrometer, amounts to about 10^{-12} M. Thus in water with the $^1O_2$ lifetime of $\tau_\Delta = 4.2$ μs[11] with our IRL spectrometer only thermal reactions can be measured, which generate $^1O_2$ with a rate of $v_{^1O_2} \geq [^1O_2]_s/\tau_\Delta \geq 2.4 \times 10^{-7}$ M·s^{-1}. However, if D_2O is used as a solvent instead of H_2O, then reactions with a lower $v_{^1O_2}$ value ($v_{^1O_2} \geq 1.5 \times 10^{-8}$ M·s^{-1}) can still be measured as a consequence of the longer $^1O_2$ lifetime in D_2O with $\tau_\Delta = 68$ μs.[11]

For reaction 1 catalyzed by molybdate ions in basic aqueous solution at pH = 10.5 Aubry and Cazin[4] have determined values of $v_{^1O_2} \geq 5 \times 10^{-7}$ M·s^{-1}. Thus this reaction should be measurable without difficulties with our IRL spectrometer.

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Introduction of eq II into eq I results in

$$I_P = ck_P\tau_\Delta v_{^1O_2} \qquad \text{(III)}$$

Equation III will be frequently stressed in the following.

Reaction Scheme and Rate Law. It is well established that the reaction between MoO_4^{2-} ions and H_2O_2 in neutral and alkaline media leads to two derivatives.[12] At low H_2O_2 concentration a yellow diperoxo species, MoO_6^{2-}, is formed,[12-17] whereas for a large excess of H_2O_2 a red-brown tetraperoxo molybdate, MoO_8^{2-}, is generated.[12,18,19]

In principle $^1O_2$ can be produced by the decomposition of both MoO_6^{2-} and MoO_8^{2-}. The mechanism of $^1O_2$ formation may therefore represented by the following steps:

$$2H_2O_2 + MoO_4^{2-} \rightleftarrows 2H_2O + MoO_6^{2-} \qquad (4)$$

$$MoO_6^{2-} \rightarrow MoO_4^{2-} + {}^1O_2 \qquad (5)$$

$$HMoO_6^{-} \rightleftarrows H^+ + MoO_6^{2-} \qquad (6)$$

$$H_2O_2 \rightleftarrows H^+ + HO_2^- \qquad (7)$$

$$2H_2O_2 + MoO_6^{2-} \rightleftarrows 2H_2O + MoO_8^{2-} \qquad (8)$$

$$MoO_8^{2-} \rightarrow MoO_6^{2-} + {}^1O_2 \qquad (9)$$

$$HMoO_8^{-} \rightleftarrows H^+ + MoO_8^{2-} \qquad (10)$$

Under the assumption that the decompositions of MoO_6^{2-} (reaction 5) and of MoO_8^{2-} (reaction 9) are slow compared with the attainment of the equilibria 4, 6–8, and 10, the rate law for $^1O_2$ formation is

$$v_{^1O_2} = \{(k_5 + \{k_9K_8[H_2O_2]_0^2\}/A)[MoO_4^{2-}]_0[H_2O_2]_0^2\}/ \\ \{(K_4)^{-1}A + (1 + [H^+]/K_6)[H_2O_2]_0^2 + \\ (\{1 + [H^+]/K_{10}\}K_8[H_2O_2]_0^4)/A\} \qquad \text{(IV)}$$

Here $A = (1 + K_7/[H^+])^2$, $[MoO_4^{2-}]_0$ denotes the starting concentration, $[H_2O_2]_0$ is the total concentration of free hydrogen peroxide, k_5 and k_9 represent the rate constants of reactions 5 and 9, respectively, and K_i are the constants of the equilibria 4, 6–8, and 10, whereby the constants K_4 and K_8 contain the constant water concentration.

Aubry and Cazin[4] have measured $v_{^1O_2}$ values of the MoO_4^{2-}-catalyzed disproportionation of H_2O_2 with dependence upon pH ($8 \le pH \le 13$) and upon H_2O_2 concentration ($0.005\ M \le [H_2O_2] \le 0.11\ M$) using solutions containing 1 mM MoO_4^{2-}. Although measurements were performed with a ratio $[H_2O_2]/[MoO_4^{2-}] = 110$ at pH = 10.5, where a part of MoO_6^{2-} should be converted into MoO_8^{2-},[19] the authors found that their results can be described by eq V, indicating that, under the experimental

$$v_{^1O_2} = \frac{1}{2}v_{H_2O_2} = \frac{k_5[MoO_4^{2-}]_0[H_2O_2]_0^2}{(K_4)^{-1}A + (1 + [H^+]/K_6)[H_2O_2]_0^2} \qquad \text{(V)}$$

conditions used, MoO_8^{2-} species do not influence $v_{^1O_2}$ or the rate of disappearance of H_2O_2, $v_{H_2O_2}$, i.e. $k_5 \gg \{k_9K_8[H_2O_2]_0^2\}/A$ and $((K_4)^{-1}A + (1 + [H^+]/K_6)[H_2O_2]_0^2) \gg (\{1 + [H^+]/K_{10}\}K_8[H_2O_2]_0^4)/A$. The values of the rate constant and equilibrium constants in eq V are $k_5 = 4.6 \times 10^{-3}\ s^{-1}$, $K_4 = 2.5 \times 10^3\ M^{-2}$, $K_6 = 7.9 \times 10^{-10}$ M, and $K_7 = 2.5 \times 10^{-12}$ M.[4]

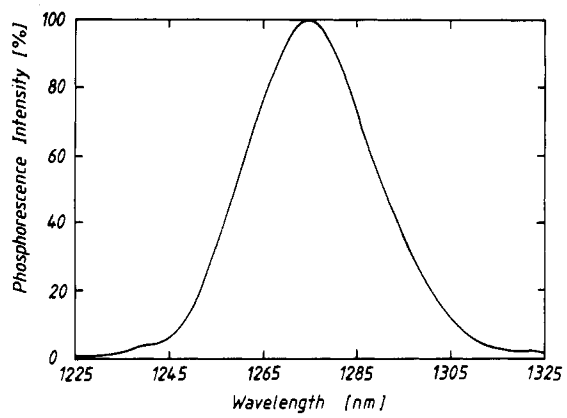

Figure 1. Phosphorescence spectrum of $^1O_2$ ($^1\Delta_g, v = 0 \rightarrow {}^3\Sigma_g^-, v = 0$). Conditions: 50 mM MoO_4^{2-}; 0.9 M H_2O_2 at $t = 0$ s; 0.5 mM EDTA; pH = 10.5; 0.2 M phosphate buffer (Na_2HPO_4/Na_3PO_4); $T = 25$ °C; half-bandwidth of emission monochromator, $\lambda_{1/2} = 34$ nm.

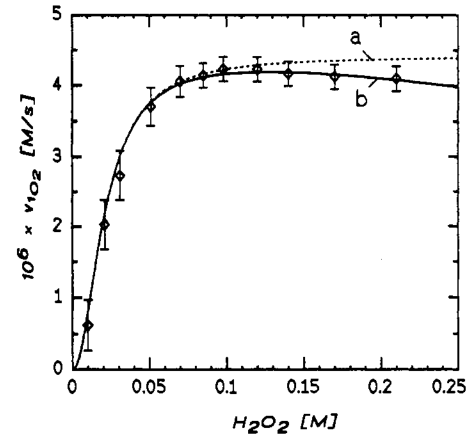

Figure 2. I_P as a function of H_2O_2 concentration. Conditions: 1 mM MoO_4^{2-}; 0.1 mM EDTA, pH = 10.5; 0.2 M phosphate buffer $T = 25$ °C. Curve a represents the theoretical curve of $v_{^1O_2}$ calculated from eq V using the rate and equilibrium constants given in the text. Curve b represents the theoretical curve of $v_{^1O_2}$ calculated from eq VI using $K_8 = 2.0\ M^{-2}$. The rhombs represent experimental values of I_P (au).

The value of $v_{^1O_2}$ strongly depends on pH and exhibits a maximum value at pH = 10.5. Thus in general, with the IRL technique, measurements were performed in solutions at about pH = 10.5.

Results and Discussion

To suppress the decomposition of H_2O_2 by impurities, EDTA was added to the solutions. Preliminary tests of the MoO_4^{2-}-catalyzed disproportionation of H_2O_2 with the IRL technique have unequivocally shown that $^1O_2$ is produced in this reaction, as demonstrated by measurements of its infrared phosphorescence spectrum (Figure 1). In order to check the results reported by Aubry and Cazin,[4] the following measurements were conducted.

$^1O_2$ Phosphorescence Emission as a Function of $[H_2O_2]$. According to eq III I_P is directly proportional to the rate of $^1O_2$ formation, $v_{^1O_2}$. From eq V it can be deduced that at $[H_2O_2]_0 \le 10^{-3}$ M ($(K_4)^{-1} \gg [H_2O_2]_0^2$) $v_{^1O_2}$ should increase with $[H_2O_2]_0^2$ and at $[H_2O_2]_0 \ge 10^{-1}$ M ($[H_2O_2]_0^2 \gg (K_4)^{-1}$) $v_{^1O_2}$ should be zero order with respect to H_2O_2. However our results are not in accordance with these expectations. In Figure 2 the dependence of I_P on $[H_2O_2]_0$ up to 0.21 M of solutions 1 mM in MoO_4^{2-} at pH = 10.5 is depicted. As can be seen, the experimental I_P values obtained for $[H_2O_2]_0 \le 0.10$ M fit very well the curve of $v_{^1O_2}$ calculated from eq V employing the values of k_5 and the various equilibrium constants mentioned above (curve a).

However, the values of I_P obtained for solutions with $[H_2O_2]_0 \ge 0.14$ M deviate distinctly from curve a which suggests that

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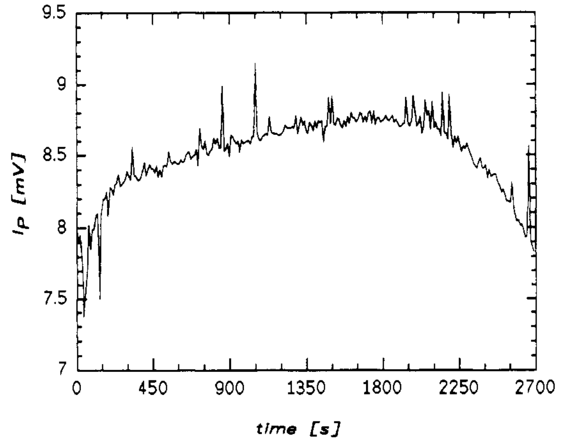

Figure 3. I_P as a function of time. Conditions: 9.3 mM MoO_4^{2-}; 0.32 M H_2O_2 at t = 0 s; 0.1 mM EDTA; pH = 10.5; 0.2 M phosphate buffer; T = 25 °C.

besides MoO_6^{2-} also MoO_8^{2-} is formed. A reasonable explanation for the decrease of I_P observed for H_2O_2 concentrations above 0.14 M is that the decomposition of MoO_8^{2-} (reaction 9) does not lead to significant $^1O_2$ formation. With the value $K_{10} = 1 \times 10^{-8}$ M reported by Dedman et al.,[20] the inequality $[H^+]/K_{10} \ll 1$ holds in the range $10.2 \leq pH \leq 10.7$. Also with the presumption that the inequality $k_5 \gg \{k_9K_8[H_2O_2]_0^2\}/A$ holds, curve b in Figure 2 was calculated from eq VI with $K_8 = 2.0$ M^{-2}.

$$v_{^1O_2} = \frac{k_5[MoO_4^{2-}]_0[H_2O_2]_0^2}{(K_4)^{-1}A + (1 + [H^+]/K_6)[H_2O_2]_0^2 + K_8[H_2O_2]_0^4/A} \tag{VI}$$

Curve b fits the experimental values of I_P better than curve a. Our results are consistent with the assumption that MoO_8^{2-} species are formed at pH = 10.5 in solutions 1 mM in MoO_4^{2-} in the range $0.10 \leq [H_2O_2] \leq 0.21$ M but that under these conditions the decomposition of MoO_8^{2-} (reaction 9) can be neglected compared with the decomposition of MoO_6^{2-} (reaction 5). The decrease of $v_{^1O_2}$ and therefore of I_P is caused by the attainment of equilibrium 8, i.e. by the contribution of the third term in the denominator of eq VI.

From curve b can be deduced that $v_{^1O_2}$ and accordingly I_P should markedly increase with increasing time for solutions with $[H_2O_2]_0 \geq 0.20$ M. Figure 3 shows for example the variation of I_P of solutions 9.3 mM in MoO_4^{2-} at pH = 10.5 with a starting concentration of $[H_2O_2]_0 = 0.32$ M. Actually, I_P increases monotonically from about 7.95 mV at reaction zero time to a value of about I_P = 8.75 mV after 1500 s and then I_P remains nearly constant over a period of about 600 s in accordance with eq VI.

$^1O_2$ Phosphorescence Emission as a Function of $[MoO_4^{2-}]$. Measurements of $v_{H_2O_2}$ show that $v_{H_2O_2}$ is first order with respect to MoO_4^{2-} in the range 0.2–2.0 mM.[21] The reaction order of $v_{^1O_2}$ with respect to MoO_4^{2-} can be determined by measuring I_P as a function of $[MoO_4^{2-}]_0$. Measurements were performed at pH = 10.5 and $[H_2O_2]_0 = 0.165$ M in the range 0.97–10.0 mM MoO_4^{2-}. Under these conditions expression VII deduced from eqs III and VI should hold true.

$$I_P = ck_P\tau_\Delta k_5 0.906[MoO_4^{2-}]_0 \tag{VII}$$

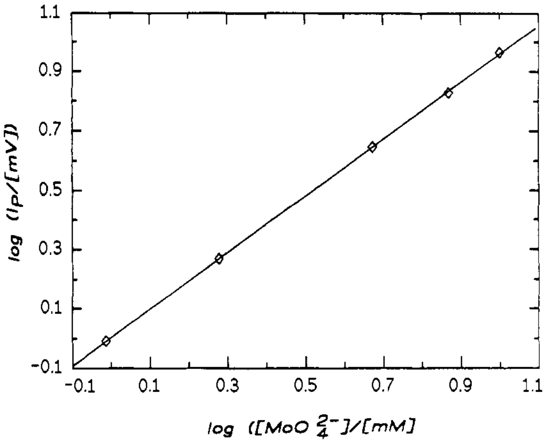

Figure 4. Double logarithmic plot of I_P versus $[MoO_4^{2-}]$. Conditions: 0.1 mM EDTA; $[H_2O_2]_0 = 0.165$ M; pH = 10.5; 0.2 M phosphate buffer; T = 25 °C.

In order to determine experimentally the exponent of $[MoO_4^{2-}]_0$ a double logarithmic plot of I_P vs $[MoO_4^{2-}]_0$ was conducted (Figure 4).

The slope of the straight line in Figure 4 is 0.97 ± 0.04, indicating that $v_{^1O_2}$ is actually first order with respect to MoO_4^{2-} in the concentration range 0.97–10.0 mM. Similar results are obtained at $10.2 \leq pH \leq 10.7$ and $0.10\ M \leq [H_2O_2]_0 \leq 0.32$ M.

The data given in Figure 4 can be used for the calculation of the constant c of our IRL spectrometer.

According to eq VII a plot of I_P vs $[MoO_4^{2-}]$ yields a straight line. From the slope SL of the straight line

$$SL = ck_P\tau_\Delta k_5 0.906 = 0.91$$

c can be calculated using the values for k_P, τ_Δ, and k_5 mentioned above. Taking into account all data of the measurements of I_P vs $[MoO_4^{2-}]_0$ (vide supra) the mean value is $c = (3.0 \pm 0.2) \times 10^8$ V·M^{-1}·s.

The knowledge of c enables us to determine directly the rate of $^1O_2$ formation (eq III) or the stationary concentration $[^1O_2]_s$ (eq I) for a given thermal $^1O_2$ source, if I_P is measured in volts. For aqueous solutions $v_{^1O_2}$ can be calculated by expression VIII.

$$v_{^1O_2} = (4.4 \pm 0.3) \times 10^{-3} I_P \ (M{\cdot}s^{-1}) \tag{VIII}$$

With $c = 3.0 \times 10^8$ V·M^{-1}·s the values of I_P at reaction time zero ($I_P \approx 7.95$ mV) and at t = 1500 s ($I_P \approx 8.75$ mV) given in Figure 3 can be evaluated using, for t = 0 s, $[H_2O_2]_0 = 0.32$ M and, for t = 1500 s, $[H_2O_2]_t = 0.13$, at which the maximum value of I_P is expected according to eq VI. At t = 0 s eq IX holds

$$I_P = 0.82ck_P\tau_\Delta k_5 9.3 \times 10^{-3} = 7.93 \text{ mV} \tag{IX}$$

and at t = 1500 s I_P is given by

$$I_P = 0.91ck_P\tau_\Delta k_5 9.3 \times 10^{-3} = 8.80 \text{ mV} \tag{X}$$

The good agreement between experimental and calculated values of I_P confirms the assumption that at H_2O_2 concentrations lower than 0.32 M the decomposition of MoO_8^{2-} (reaction 9) does not significantly contribute to $^1O_2$ formation.

Yield of $^1O_2$ formation ($y_{^1O_2}$). In accordance with reaction 1 Aubry and Cazin[4] have obtained for $y_{^1O_2}$ a value of 0.5, indicating the formation of one $^1O_2$ molecule per two molecules of H_2O_2. $y_{^1O_2}$ is given by

$$y_{^1O_2} = \frac{n_{\Delta,t}/V}{[H_2O_2]_0 - [H_2O_2]_t} \tag{XI}$$

Here $n_{\Delta,t}$ denotes the total number of moles of $^1O_2$ formed at time t, V is the sample volume, and $[H_2O_2]_0 - [H_2O_2]_t$ represents the concentration loss of H_2O_2 at time t.

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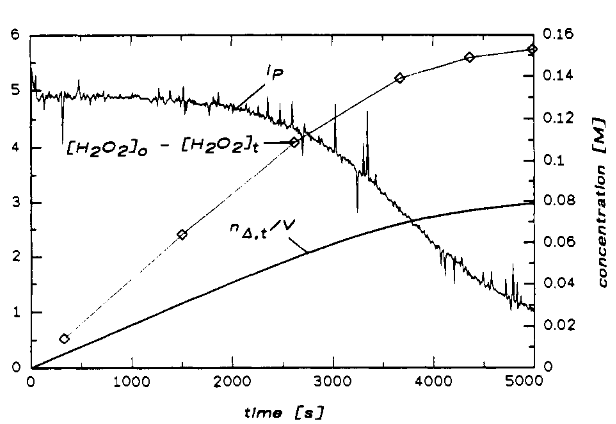

Figure 5. I_P, concentration $n_{\Delta,t}/V$, and H_2O_2 concentration loss versus time. Conditions: 5.1 mM MoO_4^{2-}; 0.1 mM EDTA; 0.165 M H_2O_2 at t = 0 s; pH = 10.5; 0.2 M phosphate buffer, T = 25 °C. $n_{\Delta,t}/V$ was calculated from eq XII using the values for c, k_P, and τ_Δ given in the text. The rhombs represent the values of H_2O_2 consumption determined by iodometric titration of H_2O_2.

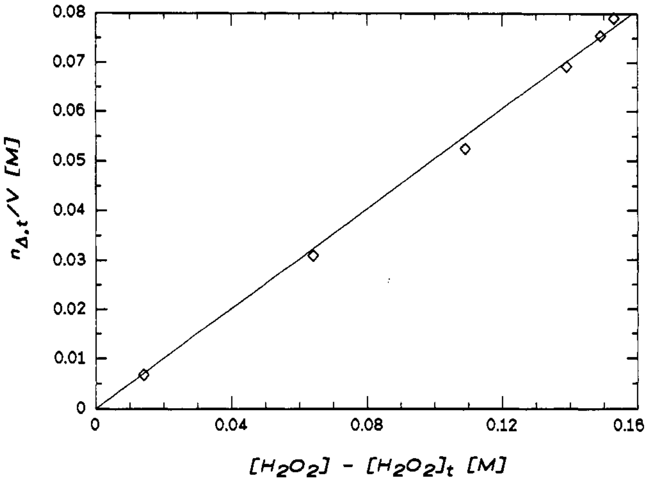

Figure 6. Plot of $n_{\Delta,t}/V$ versus $[H_2O_2]_0 - [H_2O_2]_t$. Conditions: see Figure 5.

In order to measure $n_{\Delta,t}/V$ the integrated intensity $(I_P)_t^{in}$ from the reaction from zero time until time t was measured. From the integrated form of eq III for $n_{\Delta,t}/V$ eq XII follows.

$$n_{\Delta,t}/V = \frac{1}{ck_P\tau_\Delta}(I_P)_t^{in} \qquad \text{(XII)}$$

Figure 5 summarizes the results of measurements of a solution 5.1 mM in MoO_4^{2-} and an initial concentration of $[H_2O_2]_0$ = 0.165 M at pH = 10.5. Figure 5 shows the experimental curve of I_P as a function of time, the values of $n_{\Delta,t}/V$ calculated from eq XII employing the values of c, k_P, and τ_Δ mentioned above and finally the values of $[H_2O_2]_0 - [H_2O_2]_t$ determined by iodometric titration at six different times.

As reported by Aubry and Cazin,[4] the rate of $^1O_2$ formation should be half the rate of H_2O_2 disappearance ($v_{^1O_2} = {}^1/_2 v_{H_2O_2}$). If this is true the plot of $n_{\Delta,t}/V$ vs $[H_2O_2]_0 - [H_2O_2]_t$ according to eq XI should yield a straight line with a slope of SL = $y_{^1O_2}$ = 0.50.

$n_{\Delta,t}/V$ is plotted versus $[H_2O_2]_0 - [H_2O_2]_t$ in Figure 6. The slope of the straight line is SL = $y_{^1O_2}$ = 0.51 ± 0.03, confirming the result of Aubry and Cazin.

$^1O_2$ Phosphorescence Emission at Different Temperatures. In order to eliminate the influence of the third term on $v_{^1O_2}$ (eq VI) and accordingly on I_P, we have used for measurements of I_P as a function of temperature solutions 9.5 mM in MoO_4^{2-} and 0.093 M in H_2O_2 at pH = 10.5. Under these conditions also the first term in eq VI can be neglected compared with the second.

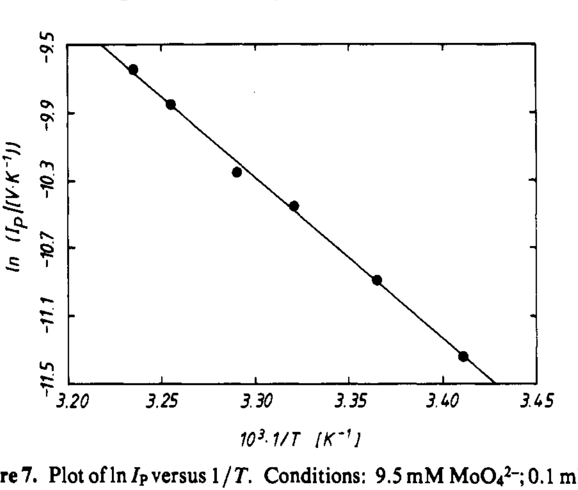

Figure 7. Plot of ln I_P versus $1/T$. Conditions: 9.5 mM MoO_4^{2-}; 0.1 mM EDTA; $[H_2O_2]_0$ = 0.093 M; pH = 10.5; 0.2 M phosphate buffer.

Accordingly, I_P is given by

$$I_P = ck_P\tau_\Delta[MoO_4^{2-}]_0k_5/(1 + [H^+]/K_6) \qquad \text{(XIII)}$$

The temperature dependence of I_P should be mainly caused by the temperature dependence of k_5. The constants c, k_P, and τ_Δ can be regarded as temperature independent,[22] and the temperature dependence of $[MoO_4^{2-}]_0$ and of $[H^+]/K_6 \ll 1$, respectively, should be neglected compared with the temperature dependence of k_5.

Figure 7 shows the corresponding Arrhenius plot. The calculated kinetic data are E_a = 15.6 ± 1.2 kcal·mol^{-1} and log A = 9.1 ± 0.9, whereby log A was evaluated from the Arrhenius equation employing the value of E_a and the rate constant k_5 = 4.6 × 10^{-3} s^{-1} at T = 25 °C. The activation energy agrees within experimental error with the value E_a = 17.6 ± 1.0 kcal·mol^{-1} reported for the decomposition of MoO_6^{2-}.[21b]

However, it is important to emphasize that the activation parameters depend on H_2O_2 concentrations. With increasing H_2O_2 concentration E_a increases. For solutions 10 mM in MoO_4^{2-} at pH = 10.5 with $[H_2O_2]_0$ = 0.16 M and $[H_2O_2]_0$ = 0.47 M, respectively, we obtained excellent Arrhenius plots. The calculated values of E_a are 17.3 ± 1.3 and 19.2 ± 1.0 kcal·mol^{-1}, respectively. A reasonable explanation for this increase of E_a is that at H_2O_2 concentrations above 0.10 M the temperature dependence of I_P is caused not only by the temperature dependence of the rate constant k_5 but also by that of the equilibrium constant K_8 (see eq VI).

Concluding Remarks

The formation of $^1O_2$ in a thermal reaction can be unequivocally proved by the infrared luminescence (IRL) of $^1O_2$ at 1270 nm.

The system H_2O_2/MoO_4^{2-} is a very efficient $^1O_2$ source and is most suitable for calibration of a home-built IRL spectrometer.

At the present time the IRL method is limited in water to thermal reactions which produce $^1O_2$ with a rate $v_{^1O_2}$ = 2 × 10^{-7} M·s^{-1} (H_2O) or $v_{^1O_2}$ = 1.5 × 10^{-8} M·s^{-1} (D_2O). Thus it seems unlikely that biochemical reactions generating $^1O_2$ can be measured by the IRL method under in vivo conditions.

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