

Singlet Molecular Oxygen Generation from the Decomposition of Sodium Peroxotungstate and Sodium Peroxomolybdate

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Singlet oxygen is formed by thermal decomposition of peroxomolybdates and peroxotungstates in basic aqueous solution. As shown by both infrared chemiluminescence and chemical trapping, the yield of $^1\text{O}_2$ released by this system is a total of about 160% (80% based on O_2 released). The infrared chemiluminescence technique is particularly useful for studying reaction kinetics in this system.

Introduction

There are many methods for generating $^1\text{O}_2$ in water, most of which are dependent on reactions of hydrogen peroxide or peroxyacids.¹⁻⁵ Unfortunately, oxidation of the substrate by these powerful oxidants often complicates the singlet oxygen reaction. Naphthalene endoperoxides provide highly useful chemical sources of singlet oxygen for mechanistic studies since they give known quantities of pure $^1\text{O}_2$ when warmed at moderate temperature (30–50 °C).^{6,7} However, such organic peroxides may create problems because of their poor stability in the presence of metal ions and their low solubility in water.

Peters et al. reported that potassium perchromate undergoes decomposition with formation of singlet oxygen in aqueous solution.⁸ An upper limit for the yield of singlet oxygen was estimated to be only 6%. Since this reaction produces superoxide and hydroxide ion along with singlet oxygen, it has not found much use as a chemical source of singlet oxygen. Aubry recently showed that MoO_4^{2-} reacts catalytically with H_2O_2 in basic aqueous solution to form $^1\text{O}_2$ in quantitative yield through the intermediacy of a diperoxomolybdate anion, MoO_6^{2-} .⁹⁻¹¹ In this paper, we report that several relatively stable peroxomolybdates and tungstates decompose to give $^1\text{O}_2$ at 30–60 °C in high yield. The production of singlet oxygen and the reaction kinetics were directly monitored by detection of the infrared chemiluminescence of singlet oxygen using a sensitive liquid-nitrogen-cooled germanium photodiode (see Experimental Section). After this work was completed, we received a paper reporting similar work with nearly identical conclusions carried out by Böhme and Brauer.¹²

Results

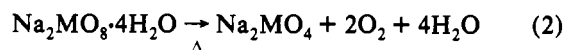
Synthesis and Characterization. Sodium peroxotungstate and peroxomolybdate have been prepared by a number of workers in

neutral or slightly alkaline solutions with the following stoichiometry (review¹³).



We prepared these compounds by Jahr's method.¹⁴ Pure crystalline products were collected by the addition of acetone to the reaction mixture at 0 °C.¹⁵ The peroxide content of these compounds was determined by measuring the oxygen evolved on heating (see Experimental Section). Water loss was also determined. The results are shown in Table I.

As reported,¹³ these compounds give almost 2 mol of O_2/g -atom of molybdenum or tungsten on thermal decomposition (eq 2), leaving a residue of molybdate or tungstate; they are believed



to contain four peroxy groups per metal atom, corresponding to the formula MO_8^{2-} . It is not certain, however, that all of these peroxy groups are bound to metal. The sodium salt $\text{Na}_2\text{MoO}_8 \cdot 2\text{H}_2\text{O}$ cannot be dehydrated further without loss of peroxide, from which it was concluded that the substance contains two molecules of H_2O_2 of crystallization.¹³ On the other hand, an anhydrous potassium salt has been obtained which must contain four directly bound peroxy groups.¹³ It seems likely that the MO_8^{2-} ion exists in the solid state, though it may be readily hydrolyzed in solution with loss of oxygen.

It is believed that Na_2MO_8 decomposes through the intermediacy of Na_2MO_6 , the monomeric form of the well-defined complex $\text{M}_2\text{O}_{11}^{2-}$.^{10,11,13} In order to detect MO_6^{2-} , the decomposition of red Na_2MO_8 in D_2O was followed by UV-visible spectroscopy. MoO_8^{2-} is present in solution throughout the decomposition, as shown by the absorption at 450 nm. Because of the strong absorption of MoO_8^{2-} , no absorption corresponding to any intermediate such as MoO_6^{2-} could be detected by UV-visible spectroscopy. However, the decomposition of red peroxomolybdate in the solid state did give a yellow solid (Na_2MoO_6 ?¹⁶), which decomposes in solution to give oxygen.

From acid solutions containing alkali-metal molybdate and tungstate and a high concentration of H_2O_2 , stable alkali-metal salts of dimeric tetraperoxy-1,2-species $\text{M}_2\text{O}_{11}^{2-}[(\text{O}_2)_2\text{M}(\text{O})-$

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(16) Since only 0.7 mol of oxygen was evolved per gram atom of Mo (by gas buret with heating) this compound is probably a mixture of Na_2MoO_4 and Na_2MoO_6 . It was shown by IR emission that the oxygen evolved was $^1\text{O}_2$.

Table I. Oxygen and Water Evolved from Peroxo Complexes

sample	Trial	moles per gram atom Mo or W	
		oxygen ^a	water ^b
Na ₂ WO ₈			
1	1	1.96	3.80
	2	1.86	4.01
	3	1.94	4.07
2	1	1.97	3.91
	2	1.95	4.20
	3	1.89	3.59
av		1.93 ± 0.04	3.93 ± 0.22
Na ₂ MoO ₈			
1	1	1.96	4.07
	2	2.01	4.23
	3	1.99	4.32
av		1.99 ± 0.03	4.21 ± 0.13

^a Measured by gas buret after heating to 60 °C. ^b Determined by difference in weight after heating to 150 °C (see Experimental Section).

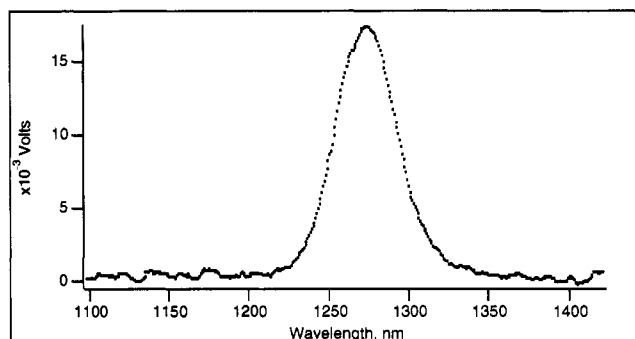


Figure 1. Chemiluminescence spectrum from the decomposition of Na₂WO₈ (0.088 M) in water (pH 10, 0.05 M borate buffer) at 40.4 °C.

OM(O)(O₂)₂²⁻ (where M is Mo or W) may be obtained.^{17,18} The structure of these complexes has been confirmed by crystallography.^{17,19} We prepared K₂Mo₂O₁₁·4H₂O and K₂W₂O₁₁·4H₂O by literature procedures.^{17,18} The UV spectrum of K₂Mo₂O₁₁·4H₂O in D₂O showed the bands reported for HMoO₆²⁻.²⁰ These bands result from a rapid equilibrium between monomeric and dimeric MoO₆²⁻ species. It is still debatable whether the stable yellow diperoxo complex is HMoO₆²⁻ or its dimer M₂O₁₁²⁻.^{13,21}

Quantitation of the Singlet Oxygen Yield. Preliminary studies showed that the oxygen produced in reaction 2 was, at least in part, O₂ (¹Δ_g), as shown by measurement of its infrared chemiluminescence spectrum (Figure 1).

We used the intensity and decay kinetics of ¹O₂ to study the mechanism of this reaction. The luminescence decays very rapidly because of the depletion of sodium peroxo compounds. The good exponential fit (Figure 2, solid line) suggests that the decomposition is first order in Na₂MO₈.

In order to measure the yield of singlet oxygen, the total integrated intensity *I*_{tot} for the reaction from zero time until completion (which is proportional to the total amount of singlet oxygen formed) was measured. For the system

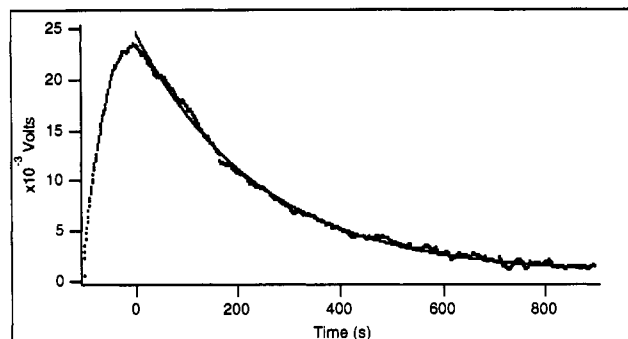
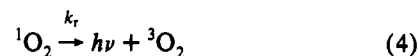
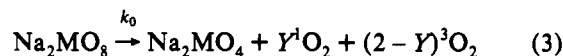


Figure 2. Singlet oxygen IR emission at 1268 nm and first-order fit of the decomposition of Na₂WO₈ (0.089 M) in water (pH 10.0, 0.05 M borate buffer) at 40.4 °C. The solid line is an exponential fit to the decay.



where *Y* is the singlet oxygen yield and *k_r* and *k_{nr}* are the radiative and nonradiative rate constants of ¹O₂ decay, the instantaneous luminescence intensity can be expressed as

$$d[h\nu]/dt = k_r[{}^1\text{O}_2]$$

With the steady-state approximation

$$d[{}^1\text{O}_2]/dt = k_0Y[\text{Na}_2\text{MO}_8] - k_r[{}^1\text{O}_2] - k_{nr}[{}^1\text{O}_2] = 0$$

or

$$[{}^1\text{O}_2] = \frac{k_0Y[\text{Na}_2\text{MO}_8]}{k_r + k_{nr}}$$

If *k_r* + *k_{nr}* = *k_d*, then the total integrated chemiluminescence intensity is

$$I_{\text{tot}} = \int_0^\infty [h\nu] = \int_0^\infty \frac{k_r k_0}{k_d} Y[\text{Na}_2\text{MO}_8]_0 \exp(-k_0 t) dt$$

or

$$E_{\text{tot}} = m \frac{k_r}{k_d} Y[\text{Na}_2\text{MO}_8]_0 \quad (6)$$

In the above equation, *m* is an instrumental constant relating voltage measured, *E*, to the light intensity, *I* (*E*_{tot} will hereafter be referred to as the IR emission integral). Equation 6 indicates that the integrated signal intensities are proportional to the initial concentration of reacting substrate. In other words, a plot of *E*_{tot} against initial peroxide concentration should give a straight line with a slope proportional to the singlet oxygen yield. Since the radiative lifetime of singlet oxygen (*k_r*/*k_d*) is solvent-dependent,^{22,23} the amount of singlet oxygen can be determined by comparing the 1268-nm luminescence intensities (*E*_{tot}) only in the same solvent with a standard of known singlet oxygen yield, as shown in eq 7. Under these conditions, the instrumental constant cancels, and

$$Y_{\text{Na}_2\text{MO}_8} = \frac{I_{\text{tot}}^{\text{Na}_2\text{MO}_8}}{I_{\text{tot}}^{\text{STD}}} \frac{[\text{STD}]_0}{[\text{Na}_2\text{MO}_8]_0} Y_{\text{STD}} \quad (7)$$

The standard chosen was the reaction of *N*-chlorosuccinimide

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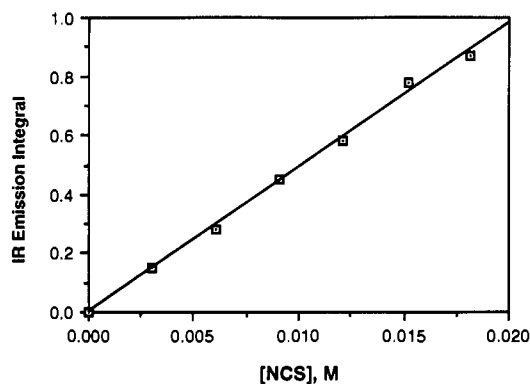


Figure 3. IR emission integral (arbitrary units) vs NCS concentration for the reaction between H_2O_2 (0.62–0.79 M) in water (pH 4.8, 0.20 M acetate buffer) at 40.4 °C.

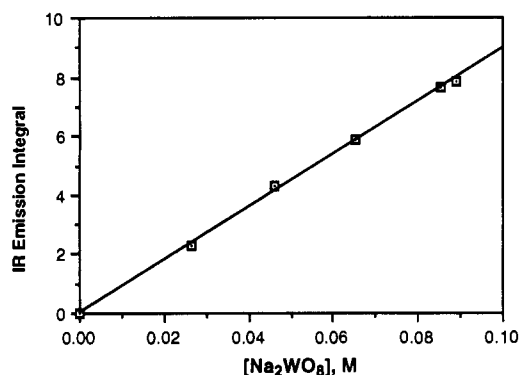


Figure 4. IR emission integral vs Na_2WO_8 concentration for the decomposition of sodium peroxotungstate in water (pH 10.0, 0.05 M borate buffer) at 40.4 °C.

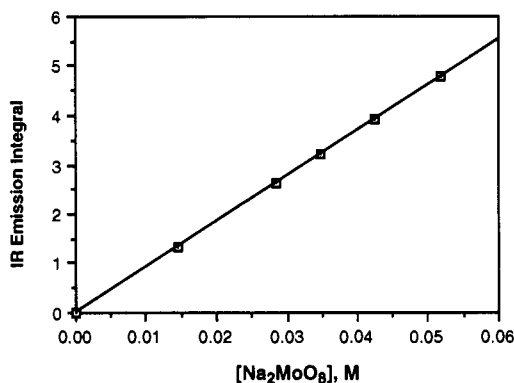
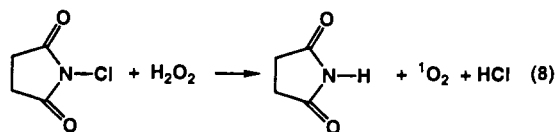


Figure 5. IR emission integral vs Na_2MoO_8 concentration for the decomposition of sodium peroxomolybdate in water (pH 10.0, 0.05 M borate) at 40.4 °C.

(NCS) and hydrogen peroxide (eq 8), for which the singlet oxygen yield is 93%.^{2,7} Figure 3 shows that the IR emission integral at 1270 nm is proportional to the concentration of NCS for this standard.



Figures 4 and 5 summarize the results for the decomposition of sodium peroxotungstate and peroxomolybdate, respectively, for which the IR emission integral is proportional to the concentration of Na_2MO_8 in water. Since the data in Figures 4 and 5 are linear over the entire range of concentrations, any

Table II. Singlet Oxygen Yield from the Decomposition of Na_2MO_8

compd	T, °C	slope, M ⁻¹	Y ± 10%
NCS + H ₂ O ₂ ^a	40.4	52.5 ± 4.8	(0.93) ^b
Na_2WO_8 ^c	30.3	89.0 ± 1.0	1.58
	40.4	94.8 ± 4.7	1.68
	50.5	94.8 ± 3.8	1.68
	60.2	87.8 ± 5.1	1.56
<i>d</i>	40.4	90.7 ± 2.1	1.61
	<i>e</i>	40.4	1170.1
Na_2MoO_8 ^c	30.3	97.6 ± 1.4	1.73
	40.4	93.8 ± 3.5	1.66
	50.3	93.8 ± 5.0	1.66
	60.7	89.9 ± 2.0	1.59
	<i>d</i>	40.4	92.2 ± 0.6
DMNO ₂ ^{f,g}	60.0	388.7	(0.76) ^b
Na_2MoO_8 ^g	60.0	341.6	0.67

^a 0.2 M phosphate or acetate, pH 4.8–6.2. ^b Standard. ^c No buffer. ^d pH 10.0 (0.05 M borate). ^e In 98% D₂O (pD 10.0, 0.10 M borate). ^f 1,4-Dimethylnaphthalene endoperoxide (standard, see refs 25 and 26). ^g In methanol.

Table III. Effect of pH on ¹O₂ Yield for the Decomposition of Na_2WO_8 in Water

pH	slope, M ⁻¹	Y ± 10%
8.6 ^a	71.9 ± 1.9	1.27
10.0 ^b	90.7 ± 2.1	1.61
10.8 ^a	70.1 ± 2.5	1.24
11.8 ^a	47.8 ± 3.1	0.85

^a 0.05 M phosphate, 40.4 °C. ^b 0.05 M borate, 40.4 °C.

contribution from side reactions such as quenching of ¹O₂ by Na_2MO_8 or Na_2MO_4 must be small in our experiments.

Using eq 7, the singlet oxygen yield can be determined by comparing the slopes of the lines in Figure 3 (standard) and Figure 4 or 5 (Na_2WO_8 or Na_2MO_8 , respectively, see Table II). The data in Table II show that the yield of singlet oxygen from decomposition of Na_2MO_8 is about 160% (based on complex) and independent of both temperature and buffer. Addition of a metal chelator such as EDTA has no effect on the yield of singlet oxygen from this system. Although Na_2MoO_8 is soluble in methanol, the yield of singlet oxygen is much lower in this solvent than that in water. The yield of ¹O₂ from the decomposition of Na_2WO_8 or Na_2MoO_8 is nearly the same.

As shown in eq 6, the slope for the plot of E_{tot} vs $[\text{Na}_2\text{MO}_8]_0$ is proportional to the lifetime of ¹O₂ with the same reacting substrate and all other factors equal. The decomposition of sodium peroxotungstate was monitored in both 98% D₂O and H₂O. As seen from Table II, the slope in D₂O is 12.9 times greater than that in H₂O, close to the difference in lifetime of the two solvents since ¹O₂ has a lifetime 14 ± 1 times longer in pure D₂O than in H₂O.^{22,24} This provides further confirmation of ¹O₂ generation from this system.

pH Effects. There is only a slight pH change during the decomposition of Na_2WO_8 . For example, while an unbuffered solution of Na_2WO_8 (0.056 M) had a pH of 10.5 after 1 h at room temperature, the totally decomposed solution had a pH of 10.1. However, there is a dramatic decrease in the singlet oxygen yield when the reaction is run in more basic or more acidic solution, as shown in Table III. These observations are consistent with the results of Aubry's work.^{10,11} If the reaction medium is too basic, hydrogen peroxide dissociates and the singlet oxygen reaction stops, probably because HOO⁻ degrades, giving a lower yield of ¹O₂.⁵ If the medium is too acidic, the peroxotungstate or peroxomolybdate will dimerize to produce the stable tetraperoxy-1,2-species $[(\text{O}_2)_2\text{M}(\text{O})\text{OM}(\text{O})(\text{O}_2)_2]^{2-}$ with a decrease of ¹O₂ production.

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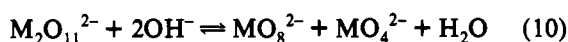
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Table IV. Singlet Oxygen Yield from the Decomposition of Diperoxo Complexes at 60 °C

compd	pH	slope, M ⁻¹	Y ± 10%
Na ₂ WO ₈ ^a	10.0 ^b	89.1	1.57
K ₂ Mo ₂ O ₁₁	9.2–9.8 ^b	89.2	1.57
	7.0 ^c	11.9	0.21 ^d
K ₂ W ₂ O ₁₁	9.2–9.8	85.9	1.51
	7.0	e	0.30 ^{d,e}

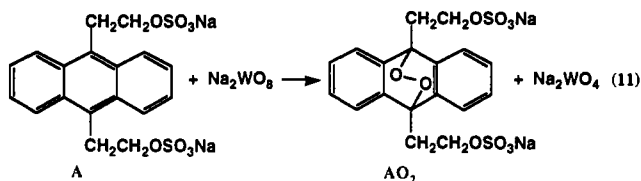
^a Standard (see next section). ^b 0.05 M borate. ^c 0.05 M phosphate. ^d Yield dependent on buffer concentration, Y < 0.05 if no buffer is used. ^e In D₂O (pD 7.0, 0.2 M phosphate) using IR emission integral and K₂Mo₂O₁₁ as standard.

Studies on M₂O₁₁²⁻. Although both K₂Mo₂O₁₁ and K₂W₂O₁₁ are very stable below pH 7, they decompose easily in basic solution, probably through the intermediacy of MO₆²⁻ or MO₈²⁻^{13,21} to produce singlet oxygen in high yield.



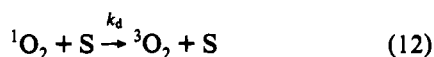
The IR emission integral from these salts is also proportional to their concentration, and the quantitative results are shown in Table IV.

Chemical Detection of Singlet Molecular Oxygen. The generation of ¹O₂ from the decomposition of Na₂WO₈ was also monitored by chemical trapping with sodium 9,10-bis(2-ethylene)anthracene disulfate (A).^{7,27} Formation of AO₂ and loss of A were detected by HPLC.⁷



When ¹O₂ is produced in the presence of a trap A, it can disappear by three pathways: quenching by solvent (*k_d*), quenching by A (*k_q*), or reaction with A (*k_r*).

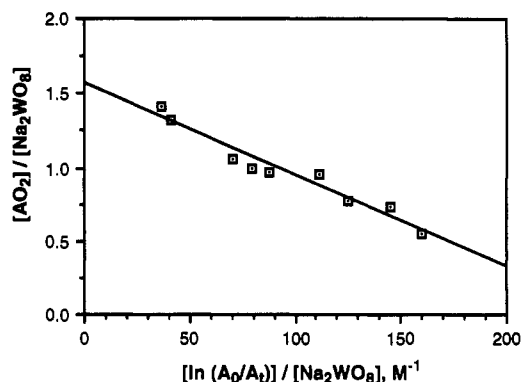
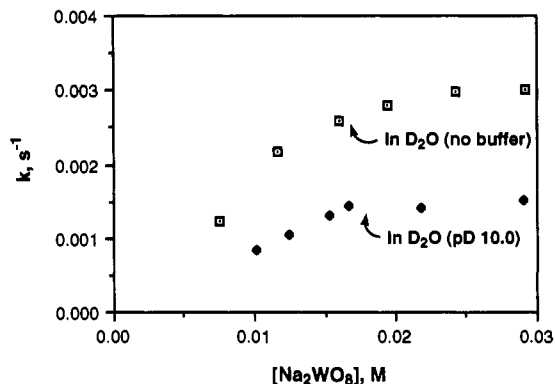
Scheme I. Pathways for ¹O₂ Decay in the Presence of Trap A



We measured the singlet oxygen yield ($Y = [^1O_2]/[Na_2WO_8]$) using this trap with various concentrations of acceptor A using Aubry's method²⁸ and eq 15, where $\beta = k_d/(k_r + k_q)$, $\gamma = k/(k_r + k_q)$

$$\frac{[AO_2]}{[Na_2WO_8]} = -\beta \frac{\ln(A_0/A_t)}{[Na_2WO_8]} + \gamma Y \quad (15)$$

+ *k_q*), and AO₂ is the yield of anthracene endoperoxide (eq 11). Representative data are given in Figure 6, and the extrapolated singlet oxygen yield ($Y = 1.57 \pm 0.06$) is very close to that determined by chemiluminescence (*k_q* was assumed to be zero

**Figure 6.** Chemical trapping of singlet molecular oxygen from the decomposition of Na₂WO₈ in water (pH 10.0, 0.05 M borate) at 40.4 °C.**Figure 7.** Rate constant for the decomposition of sodium peroxotungstate vs concentration in deuterium oxide at 40.4 °C.**Table V.** Rate Constants for Decomposition of Na₂WO₈ and Na₂MoO₈ at 40 °C

compd	10 ³ k, s ⁻¹	
	H ₂ O	H ₂ O (pH 10.0) ^a
Na ₂ WO ₈	3.22 ± 0.21	3.41 ± 0.39
Na ₂ MoO ₈	7.50 ± 0.46	6.92 ± 0.53

^a 0.05 M borate.

here); the slope, $k_d/k_r = (6.20 \pm 0.55) \times 10^{-3} M$ is also in good agreement with the value determined by Di Mascio et al. ($7.7 \times 10^{-3} M$ at 37 °C).⁷

Kinetic Study of the Decomposition of Na₂MoO₈. The pseudo-first-order rate constant for decomposition of sodium peroxotungstate was monitored by the luminescence of singlet oxygen at 1270 nm (Figure 2). Figure 7 shows that the pseudo-first-order rate constant for decomposition of sodium peroxotungstate in D₂O, monitored by the luminescence of singlet oxygen at 1270 nm (Figure 2), is independent of concentration at $[Na_2WO_8] \geq 0.02 M$ but dependent on the concentration at lower concentrations. In order to eliminate this effect, concentrations of Na₂WO₈ above 0.02 M where the decomposition is first-order were used.

Table V summarizes the rate constants for Na₂MoO₈ decomposition at 40 °C in water. As seen in Table V, the rate constant changes slightly in buffered water.

The activation parameters for the decomposition of Na₂WO₈ and other peroxides were measured by determination of the dependence of rate constants on temperature by ¹O₂ chemiluminescence; Figure 8 is an Arrhenius plot for the decomposition of sodium peroxotungstate. Values determined are shown in Table VI. Because of the weak IR signal for the decomposition of K₂Mo₂O₁₁ at pH 7.0, the activation energy was determined from measurements of the initial light emission from the same solution

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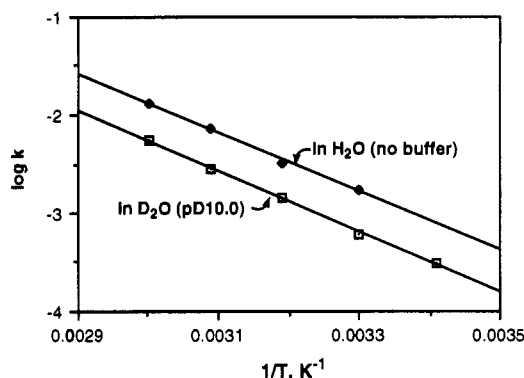


Figure 8. Arrhenius plot for the decomposition of Na_2WO_8 .

Table VI. Kinetic Data^a for the Decomposition of Peroxo Complexes

compd	solvent	log <i>A</i>	<i>E</i> _a , kcal mol ⁻¹	<i>R</i> ²
Na_2WO_8	H_2O	7.0	13.5	0.995
	D_2O^b	7.0	14.1	0.999
Na_2MoO_8	H_2O	5.1	10.4	0.999
	D_2O^b	5.8	11.4	0.993
$\text{K}_2\text{Mo}_2\text{O}_{11}^c$	D_2O^d	10.2	17.8	0.991

^a 30–60 °C; ±10% estimated on the basis of IR emission measurements. ^b pD 10.0, 0.1 M borate. ^c Temperature jump results. ^d pD 7.0, 0.2 M phosphate.

at two temperatures with a short time period.²⁹ The activation energy (17.8 kcal mol⁻¹) determined for the decomposition of $\text{K}_2\text{Mo}_2\text{O}_{11}$ agrees well with the value 17.6 ± 1.0 kcal mol⁻¹ reported for the decomposition of Na_2MoO_6 .³⁰ However, the same activation energy has been reported for the decomposition of Na_2MoO_8 .³⁰

Discussion

The results of these studies show that sodium peroxotungstate and sodium peroxomolybdate in basic water (with or without buffer) are excellent chemical sources of singlet oxygen in aqueous systems. The yields of singlet oxygen are around 160%, based on the complex (~80% based on oxygen). Chemical trapping of singlet oxygen confirms these values, and the dependence of luminescence intensity on solvent deuteration is as expected for a singlet oxygen reaction. The reason that the yield is less than quantitative is not certain; it may well be caused by the decomposition of H_2O_2 , as suggested by Aubry.^{9,11}

The change in reaction order for the decomposition from first to second order at low concentrations of Na_2WO_8 in Na_2WO_8 has not been previously reported. Some, but not all, of this effect is caused by pH change, as is shown by the smaller effect in buffered D_2O . We have not investigated this complication further so far.

The relative rate constants for reaction of the peroxotungstates and peroxomolybdates depend on temperature. Although the rate constants are similar at 40 °C, the peroxotungstates have a higher activation energy and react faster at higher temperatures.

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(30) Baxendale, J. H. *Adv. Catal.* **1952**, *4*, 31–86.

Besides the high yield of singlet oxygen produced, Na_2WO_8 is very easily prepared and has high solubility in water. The yield of singlet oxygen produced in this process is the highest so far reported from chemical sources and provides a preparatively useful sources of $^1\text{O}_2$ in solution.

Experimental Section

Reagents. Sodium tungstate and molybdate were from Mallinckrodt Chemical Co.; 1,4-dimethylnaphthalene was from Aldrich Chemical Co. and purified by passage through a neutral alumina column. Potassium molybdate and tungstate were from Alfa Products, and 30% hydrogen peroxide was from Fisher Scientific Co. *N*-Chlorosuccinimide (Eastman) was recrystallized from warm water, mp 149–150 °C.

Instrumentation. The apparatus for detection of singlet oxygen in this study consists of a thermostated glass cuvette, an optical chopper (Stanford Research Model 540) working at 100 Hz, a 0.25 M monochromator (Jarrell-Ash) with 2000-nm slits, a liquid-nitrogen-cooled Ge photodiode detector (North Coast EO-817L), and a lock-in amplifier (Stanford Research Model 510) connected to a Macintosh Plus computer using LabView software for data acquisition. Generally, a measured amount of the compound to be studied was quickly dissolved in water, 2.0 mL of the solution was placed in the preheated cuvette, and the $^1\text{O}_2$ IR emission at 1268 nm was recorded as a function of time. Data analysis was carried out using the program Igor. In our apparatus, the emission peak appears at 1276 nm, corresponding to the wavelength of the (0,0) $^1\Delta_g \rightarrow ^3\Sigma_g^-$ transition of molecular oxygen (shifted from the true position at 1268 nm by the combined errors of detector sensitivity and slow time response during the scan).

Synthesis. Sodium peroxomolybdate and sodium peroxotungstate were prepared by the literature procedures in variable yields (usually over 70%).^{14,15} These coordinated peroxo compounds are stable at –20 °C in the freezer and easily decompose at room temperature, especially in solution. Their peroxide content was measured by placing a sample in a weighed tube connected to a gas buret and heating to 60 °C until the evolution of oxygen ceased. The volume of oxygen was measured; it is assumed that all the peroxo oxygen appears as O_2 . The tube was finally heated at 150 °C to constant weight, and the sodium tungstate or molybdate residue was determined gravimetrically (Table I). The water was determined by difference in weight.

Potassium tetraperoxoditungstate and potassium tetraperoxodimolybdate were synthesized by the method of Fergusson and Stomberg.^{17,18}

Caution. Although we have not encountered any specific problems in the preparation of the above sodium salts, one attempt to make K_2WO_8 resulted in an explosion. Standard precautions for handling peroxides should be followed.

Sodium 9,10-bis(2-ethylene)anthracene disulfate was prepared by the method of Schaap.²⁷ Its precursor, 9,10-anthracene-2,2'-diethanol, was synthesized by Evans' method.² The yellow disulfate has an NMR spectrum identical to that reported.²⁷

1,4-Dimethylnaphthalene endoperoxide was prepared by the photo-oxygenation of 1,4-dimethylnaphthalene.^{25,26} Its purity is easily determined by the low-temperature proton NMR spectrum (CH_3 at δ 1.88 in CDCl_3).

Chemical Trapping of Singlet Oxygen. $^1\text{O}_2$ from decomposition of Na_2WO_8 was detected by the oxidation of the chemical trap (A) to the $^1\text{O}_2$ endoperoxide product (AO_2). A reversed-phase HPLC column (C_{18}) was used to separate A and AO_2 . The mobile phase consisted of 70% aqueous ammonium acetate solution (0.1 M) and 30% methanol.⁷ The flow rate was 2.0 mL/min and UV detection was at 220 nm. Standard AO_2 solutions were prepared by irradiating oxygen-saturated solutions of A containing a trace of Rose Bengal with a 300-W Xenon lamp.

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