

GAS PHASE CHEMILUMINESCENCE FROM ALKALI
SUPEROXIDES IN SOLVENT MEDIA

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I. INTRODUCTION

It has been observed that liquid scintillators containing p-dioxane or Triton X-100 show chemiluminescence in the presence of a quaternary ammonium base such as Hyamine. This chemiluminescence decays gradually over a long period of time and is probably related to the singlet oxygen ($^1\Delta_g$) generated *in situ* (Peng, 1976).

Other methods of generating singlet oxygen include mixing hypochlorite with hydrogen peroxide (Seliger, 1960), bubbling chlorine into alkaline hydrogen peroxide (Khan, Kasha, 1970), dissolving potassium perchromate in aqueous solutions (Peters *et al.*, 1975), and dissolving alkali superoxides in protic and aprotic solvents; the latter contain moisture or hydrogen ions. Chemiluminescence due to radiative transitions of singlet oxygen occurs only in gaseous oxygen (Khan, Kasha, 1964; Browne, Ogryzlo, 1964).

The lifetime of singlet oxygen has been measured directly in solution by a spectroscopic method (Merkel, Kearns, 1972a) and found to vary with the nature of the solvent, ranging from 20 μ sec in water to 200 μ sec in carbon disulfide (Merkel, Kearns, 1972b), 700 sec in carbon tetrachloride, and 1000 μ sec in Freon-11 (Long, Kearns 1975). The average times required for isolated $O_2(b^1\Sigma_g^+)$ and $O_2(a^1\Delta_g)$ molecules in the gas phase to emit a photon and relax to the $X^3\Sigma_g^-$ ground state are 12 and 3900 seconds, respectively (Krupenie, 1972). The presence of a quencher diminishes these lifetimes considerably. Merkel and Kearns (1972b) found that dipole moment

and viscosity of the solvent have no effect on the lifetime of singlet oxygen but a profound effect is observed when the solvent is deuterated.

Using a liquid scintillation spectrometer operating in the out-of-coincidence mode, we have measured the chemiluminescence generated from potassium superoxide in solvent media such as dimethyl sulfoxide, *p*-dioxane, Triton X-100, water, etc. and found the observed lifetime of the chemiluminescence considerably longer than the lifetime of single oxygen reported in solvents (Peng, 1978). Our results were complicated by the presence of fluorescent impurities in these solutions which might be sensitized to yield chemiluminescence. As decay of singlet oxygen can be measured by the luminescence in the gas phase, free of interfering fluorescent impurities in solution, this paper reports the effects of various solvents on the gas phase chemiluminescence (i.e. singlet oxygen) produced from alkali superoxides.

II. MATERIALS AND METHODS

Chemicals used for the experiments were from the following sources: potassium and sodium superoxides from Ventron-Alpha Products, Triton X-100 (scintillation grade) from Packard Instrument Company, *p*-dioxane (scintillation grade) from Eastman Chemicals, hydrogen peroxide (30%) from Mallinckrodt Chemicals, NCS solubilizer from Amersham/Searle. Hypochlorite was a commercial bleach containing 5.25% by weight of sodium hypochlorite in water.

A liquid scintillation counter equipped with single photon counting capability (Beckman LS-9000) was used. Earlier studies were performed in a liquid scintillation counter (Packard model 3300) operating in the out-of-coincidence mode. This latter instrument was later equipped with a Kel-F 4-ml flow cell (Packard) to monitor the chemiluminescence of gases, i.e., oxygen, carbon dioxide, and nitrogen from high pressure storage cylinders (Matheson).

Ordinary counting vials with the lower portion, 2 cm high from the bottom, painted black (Figure 1) were used in initial studies. Aluminum caps (obtained from Searle Analytic, Inc.) were used to cap the vials in order to minimize photoluminescence. Liquid or solution samples were introduced into the masked vials with a hypodermic syringe which passed through a small hole drilled through the center of the aluminum cap and then through a silicon septum fitted into a Teflon plate beneath it. The Teflon plate has a rim that fits snugly to the edge of the counting vial to form a good seal (Fig. 1). This half-blackened vial when tested against a scintillator

solution containing ^3H did successfully prevent photons emitted from the solution from reaching the photocathode, but for a strong chemiluminescence source, the continuity of the glass wall of the vial serves essentially as a light guide facilitating the detection of solution photons. For this reason, a different sample-containing device was employed for subsequent studies.

A black plastic insert consisting of a trimmed minivial spray-painted totally black, was used as sample container which was placed inside an ordinary sample counting vial as shown in Fig. 1. The black insert (1.4 cm dia. x 4.5 cm) was inspected before use against bright light to detect pin holes. This sample-containing arrangement permitted the gaseous product to effuse from the top of the black insert to be detected.

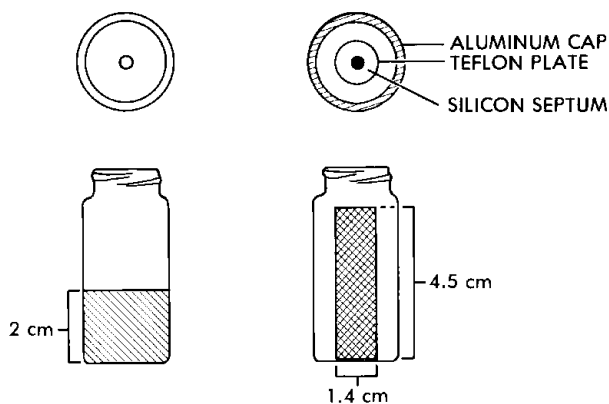


FIGURE 1. Counting vials for gas-phase chemiluminescence. Shaded sections are painted black.

Determination of the chemiluminescence from gaseous products of each reaction was carried out in the following manner. The vial and the black insert were dark adapted and counted in the single photon counting mode repeatedly for 1 minute periods for a duration of about 10 to 20 minutes to monitor the decay of background photoluminescence. Without exposing to bright or fluorescent light, potassium superoxide (~ 100 mg) was introduced into the black insert, and the increase in photo- and chemiluminescence was determined. Next, the chosen solvent (~ 2 ml) was quickly injected into the black insert, and the sample was immediately lowered into the counting chamber and counted in the single photon mode for 0.2 or 1.0 minute intervals repeatedly, depending on the decay rate of the chemiluminescence. The time lapse between the injection of the solvent and the initiation of the counting was

usually between 3 to 5 seconds. The data were plotted on semi-log paper.

Kodak Wratten Filters were wrapped around the counting vials and taped in place with thin strips of Scotch tape. These vials were used to characterize the gas phase chemiluminescence emission of potassium superoxide in 50% p-dioxane. Absorption characteristics of these filters were given in Kodak Filters (1976).

III. CHEMILUMINESCENCE

A. Chemiluminescence from Potassium Superoxide in Protic Solvents

Water, dilute p-dioxane, deuterium oxide, dilute Triton X-100, etc. generate chemiluminescence when reacted with potassium superoxide. These samples show an initial high rate of gas phase chemiluminescence which decays with a half-time characteristic of the solvent medium. The decay

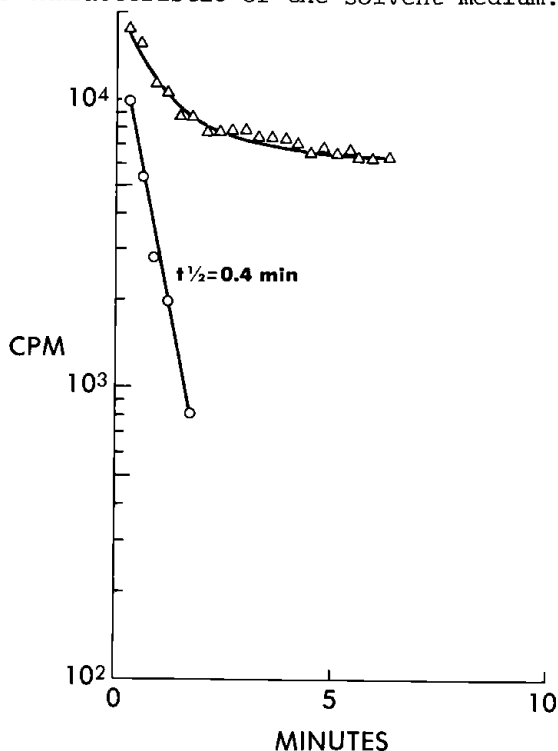


FIGURE 2. Half-time of decay of gas phase chemiluminescence from $KO_2 + H_2O$.

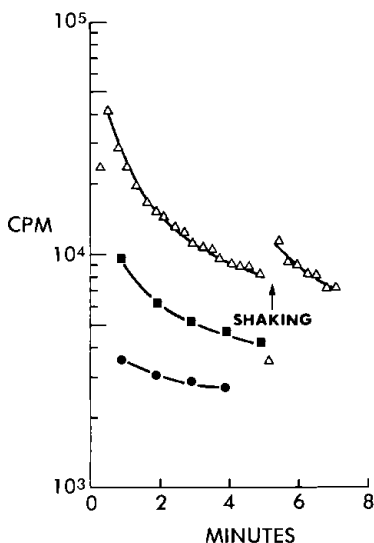


FIGURE 3. Decay of Chemiluminescence from KO_2 in 50% *p*-Dioxane. (●) Empty vial, (■) KO_2 alone (Δ) KO_2 + 50% *p*-dioxane.

curve is in general of a multicomponent shape. In water the chemiluminescence decays rapidly with a half-time for the initial and fast-decaying component approximately 0.4 minute, as shown in Fig. 2.

Figure 3 shows the decay of gas phase chemiluminescence from potassium superoxide in 50% *p*-dioxane in water. The initial component decayed with a half-time of 0.4 min and was superimposed upon the background luminescence. Gas phase luminescence was significantly increased when the content of the sample vial was agitated. Agitation apparently hastened the release of singlet oxygen from solution thereby increasing the luminescence in the gas phase. Negligible increase in photoluminescence was observed when the dark adapted vial was exposed to dim light.

Among the aqueous solvent media studied, the highest intensity of gas phase chemiluminescence was observed when potassium superoxide was mixed with Triton X-100 and water (1:1 by volume). Chemiluminescence in the gas phase from this source persisted and decayed slowly in comparison with the chemiluminescence from other solvent media containing

potassium superoxide. The half-time of the initial and fast decaying component was about 3.1 minutes, an order of magnitude greater than that in water.

B. Chemiluminescence and Deuterium Effect

One of the criteria for assessing the role of singlet oxygen is the deuterium effect on its lifetime (Merkel *et al.*, 1964b, 1964c). Deuterium oxide (D_2O) produces higher intensity of gas phase chemiluminescence from potassium superoxide than water (H_2O) (Fig. 4). The initial chemiluminescence intensity in D_2O was about 20 to 25 times that in H_2O , and the decay rate was slower by a factor of about 2.5 (i.e., 0.95 min vs. 0.4 min). A similar deuterium effect was not observed with sodium superoxide.

Since the potassium and sodium superoxides used for the experiment were reputedly to be of 96.5 and 90+ percent purity, respectively, it is likely that trace metal impurities present in the superoxides can quench the excited oxygen and nullify the deuterium effect. Composition of trace metal impurities, determined by X-ray fluorescence analysis of the alkali superoxides, is given in Table I.

TABLE I. Trace Metal Impurities in KO_2 and NaO_2 by X-ray Fluorescence

<u>Element</u>	<u>KO^b</u> <u>(ppm)</u>	<u>NaO^c</u> <u>(ppm)</u>
Cr	12	56 ± 6
Mn	9	6
Fe	20 ± 2	142 ± 14
Ni	3	26 ± 3
Cu	2 ± 1	2 ± 1
Zn	2	2 ± 1
Pb	5	5
Br	2	2
Rb	72 ± 7	2

^aRef.: Giaouque *et al.* (1973). ^bLot No. 012676 (Ventron-Alpha Products). ^cLot No. 020477 (same).

C. Chemiluminescence from Potassium Superoxide in Aprotic Solvent

Superoxide ions are stable in aprotic solvents. Figure 5 shows that when neat p-dioxane was added to potassium superoxide, practically no chemiluminescence was observed indicating that oxygen was not formed. Agitation by shaking the sample caused no increase in luminescence. Addition of a small amount of 50% p-dioxane in water raised the intensity

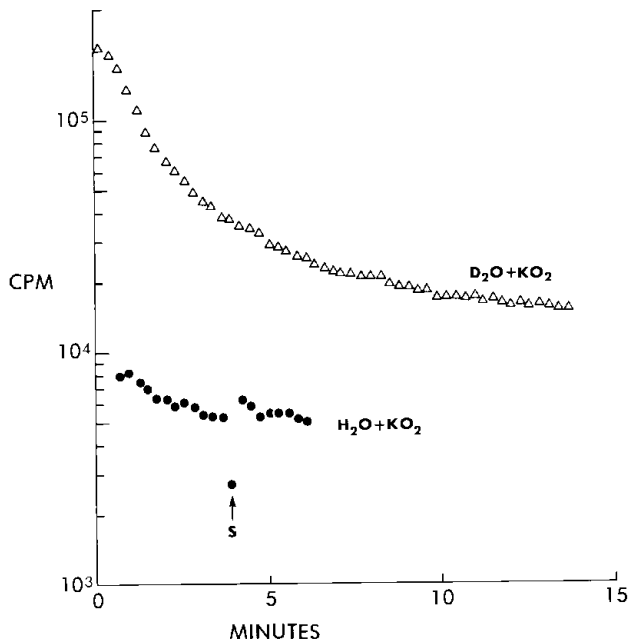


FIGURE 4. Deuterium Effect. $S \uparrow$ indicates sample being shaken and replaced.

of the chemiluminescence by several orders of magnitude over the background luminescence. The initial and fast-decaying component of the chemiluminescence had a half-time of about 0.3 minute. The chemiluminescence showed a sudden increase when the sample was agitated. This phenomenon of increased gas phase luminescence when the solution in equilibrium with the gas phase is agitated is probably caused by the escape of nascent singlet oxygen from solution. Similar phenomenon were observed with other solutions of potassium superoxide.

D. Spectral Characteristics of Chemiluminescence

The spectral characteristics of the luminescence from potassium superoxide and 50% p-dioxane were investigated with Kodak Wratten filters. Since the spectral response of

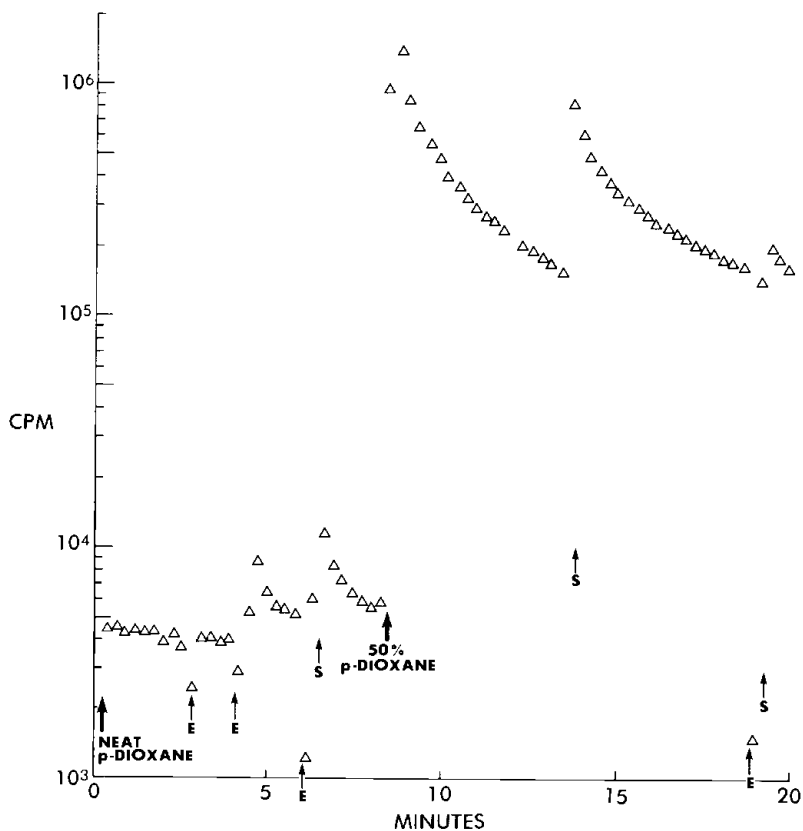


FIGURE 5. KO_2 in Neat and Dilute p-Dioxane. E↑ indicates sample elevator up; S↑ indicates sample being shaken and replaced.

the bialkali photocathode of the multiplier phototube in the liquid scintillation spectrometer is centered around 410 nm and falls off towards longer wavelength region, it is not valid to make use of the intensity of transmitted photons to characterize the emission spectrum without extensive calibration. Of the filters used (Nos. 2E, 16, 21, 25, 45, 61, 70, 98, 99) 2E gives the highest transmission. The half-time of the initial and fast decaying component, observed through filters Nos. 2E, 16, 21, 25 and 99, is about 0.39 min, which is in agreement with the half-time of singlet oxygen emission indicating that these filters pass the emission bands of

singlet oxygen. The use of filters greatly reduced the intensity of photons observed.

The maximum of the emission spectrum of the singlet oxygen ($^1\Delta_g$) occurs at 640 nm (Seliger, 1960; Khan, Kasha, 1970) and that of gaseous 1,2-dioxetanedione at 540 ± 20 nm (Stauff, Bergamann, 1972).

E. Chemiluminescence from Dioxane-based Liquid Scintillator

Figure 6 shows the decay of gas phase chemiluminescence produced from the addition of about 0.5 ml of NCS tissue solubilizer to 2 ml of dioxane-toluene based organic scintillator containing PPO, POPOP, and naphthalene. Dioxane-based scintillators are known to produce high intensity chemiluminescence upon addition of a quaternary ammonium base. The emitters have long been thought to be the scintillator molecules excited by the energy produced in the redox reaction, leading to sensitized chemiluminescence. The detection of the gas phase luminescence upon addition of the NCS reagent indicates that a gaseous emitting species, presumably singlet

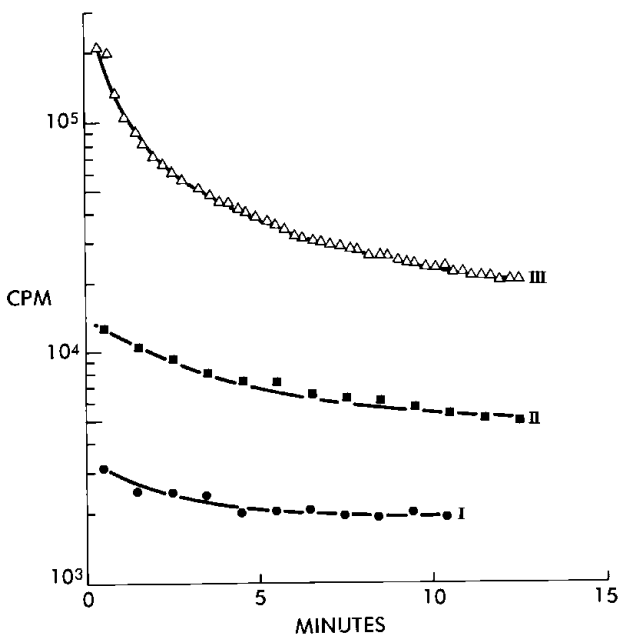


FIGURE 6. Gas-phase Chemiluminescence from Dioxane-based Liquid Scintillator upon addition of NCS solubilizer. (●) Empty vial, (■) scintillator alone, (Δ) scintillator + NCS.

oxygen, is released in the reaction. The initial and fast decaying component has a half-time of about 0.4 minute which is in agreement with that of singlet oxygen observed in other systems. The presence of other luminescent gases has not been confirmed.

F. Chemiluminescence of Gases

Luminescence produced by oxygen, carbon dioxide, a mixture of carbon dioxide and oxygen, and nitrogen when a steady stream of these gases was passed through a 4-ml Kel-F flow cell over a period of days or weeks was measured. The Kel-F flow cell was first dark adapted for several months with a constant flow of nitrogen to reach a steady background luminescence. Luminescence intensities of these gases are given in Table II.

Table II. Luminescence of Gases

<u>Gases</u>	<u>Single photon events rate (CPM)^a</u>
N ₂	1726 ± 12.7
O ₂	1996 ± 42.1
CO ₂	1767 ± 11.5
CO ₂ + O ₂	1911 ± 22.6
Air	1896 ± 15.8

^aCounts were collected over 100-minute intervals and averaged.

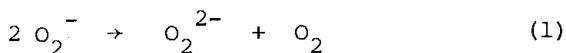
The increase in count rates of O₂, CO₂ + O₂, and air over those of N₂ and CO₂ can probably be attributed to the presence of singlet oxygen in the former gases. Other gaseous emitters such as carbon dioxide dimer (i.e., 1,2-dioxetanedione) can be formed from HCO₃⁻ in redox reactions containing CO₂, HCO₃⁻, or CO₃²⁻ (Stauff, Bergmann, 1972). The dimer was considered as a possible contributor to the gas phase chemiluminescence in this study, but the lack of

enhanced luminescence of CO_2 and $\text{CO}_2 + \text{O}_2$ over that of N_2 and an equal amount of O_2 respectively, indicates that 1,2-dioxetanedione is either not present or has decayed away. The dimer has a theoretically estimated half-time of 0.34 sec. (Richardson, O'Neal, 1972) which is about a factor of 10^4 shorter than the half-time of isolated singlet oxygen molecules.

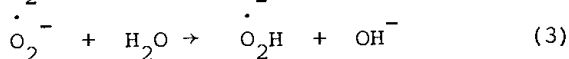
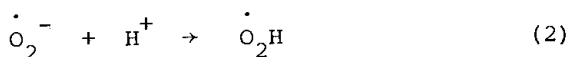
The presence of 1,2-dioxetanedione was also sought in solution in the reaction of 0.5 M NaHCO_3 with KO_2 but this exhibited no increase in gas phase chemiluminescence over that observed for H_2O and KO_2 . The absence of 1,2-dioxetanedione may be due to its rapid decay or the high energy required for its formation that the excited oxygen molecules are unable to supply by energy transfer. The singlet state of CO_2 has an energy about 140 kcal/mole above the ground state while the transition of the high energy oxygen dimols provides only 78.3 Kcal/mole.

IV. DISCUSSION

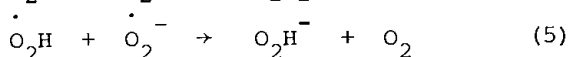
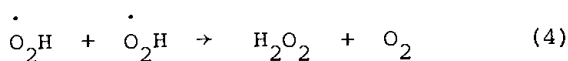
When potassium superoxide is dissolved in protic or aprotic solvents containing moisture or hydrogen ions, the excited species of oxygen ($^1\Delta_g$) is generated through the intermediary of superoxide ions. The superoxide ions do not dismutate according to eq. 1 to any detectable amount because the reaction is highly endoergic (Stauff, Bergmann, 1972; Stauff *et al.* 1972).



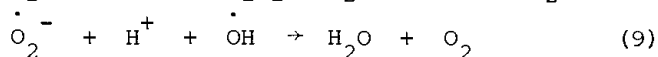
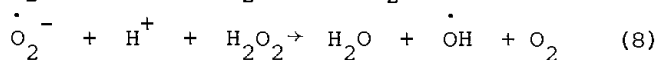
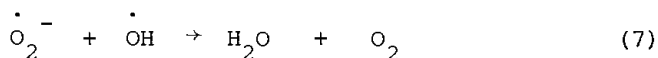
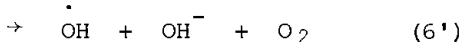
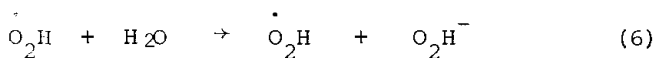
The superoxide ions react with water or protons to form perhydroxyl radicals.



These perhydroxyl radicals dismutate and react with oxygen radical ions to give singlet oxygen:



The superoxide ions may also react with H_2^+ , H_2O , and OH to form oxygen; thus



These reactions produce sufficient energy necessary for excitation of $^1\Delta_g$ state and $^1\Sigma_g^+$ state of oxygen; as a result, the oxygen formed is in the excited state. According to Khan and Kasha (1972), singlet oxygen undergoes transition as dimolecules as follows:



These transitions are characterized by their emission spectra. It may be pointed that water efficiently quenches $\text{O}_2(^1\Sigma_g^+)$ but not $\text{O}_2(^1\Delta_g)$ (Bader, Ogryzlo, 1964).

The intensity of gas phase luminescence from potassium superoxide in aqueous solutions is dependent on the nature of the solvent medium and is found to be higher in aprotic solvents containing small amount of water than in pure water. Water reacts avidly with potassium superoxide with the evolution of O_2 . The reaction is rapid and essentially complete within a matter of seconds; while in aprotic solvents, the release of O_2 is dependent upon the presence of H^+ or H_2O and may be delayed. According to Khan and Kasha (1964) and Browne and Ogryzlo (1964) radiative transition of excited oxygen molecule occur in the gas phase and in gas bubbles in aqueous matrix. In a medium consisting of surfactant molecules such as Triton X-100 and water, the gas bubbles formed are in a micellar environment which has the effect of protecting the nascent excited oxygen molecules against quenchers, thus prolonging their lifetime. Agitation hastens the formation of gas bubbles leading to an increase in gas phase chemiluminescence.

The decay of gas phase chemiluminescence is composite in nature. The initial and fast decaying component in aqueous and optically filtered systems has a half-time of 0.4 minute which is about 1/100th of the lifetime reported

for isolated $O_2(^1\Delta_g)$ molecules (Krupenie, 1972). Experimental evidence also indicates that the presence of other volatile fluorescent molecules such as 1,2-dioxetanediones is unlikely.

The slow decaying components are probably results of quasi-equilibrium conditions established between the natural decay of singlet oxygen on the one hand and the continuous generation from the solution on the other. Clear solutions of potassium superoxide in water, immediately after cessation of vigorous bubbling, can still generate gas bubbles on shaking. Aqueous Triton X-100 when in contact with potassium oxide produces a great deal of frothing. The lifetime of singlet oxygen is affected by quenching, and the reaction rate of superoxide ions in solution is affected by hydration (Khan, 1976) or other solution properties. It is not unlikely that the inordinate long lifetime of luminescence observed in solutions of potassium superoxide and the composite decay pattern of the singlet oxygen in the gas phase is a consequence of the interplay of these two opposing factors.

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