Singlet Oxygen Production in the Reaction of Potassium Superoxide with Chlorine

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The study of singlet oxygen ($^1O_2$) emission showed that the $^1O_2$ could be efficiently produced in the reaction of solid potassium superoxide (KO_2) particles with chlorine gas (Cl_2), which only occurred on the surface of solid KO_2 particles. The liquid water may accelerate the reaction of Cl_2 with KO_2 and make a complete conversion of KO_2 to $^1O_2$. The KO_2 had a similar efficiency for $^1O_2$ production as the alkali metal peroxides (such as Li_2O_2 and Na_2O_2) as reacting with Cl_2.

Potassium superoxide (KO_2) that can provide superoxide ion (O_2^-) is an important source for singlet oxygen ($^1O_2$) production through some electron-transfer reactions.[1–3] However, these reactions have a low efficiency for $^1O_2$ production and are usually used for studying the biological processes.[4] Recently, Alfano and Christe[5] identified two previously unreported gas–solid reactions for $^1O_2$ generation:

$$Na_2O_2(s) + 2HCl(g) \rightarrow 2NaCl(s) + H_2O(g) + 1/2O_2(^1\Delta_g) \quad (1)$$

$$Na_2O_2(s) + Cl_2(g) \rightarrow 2NaCl(s) + O_2(^1\Delta_g) \quad (2)$$

The solid Na_2O_2 may be replaced by other solid inorganic peroxides (such as Li_2O_2 or BaO_2), and HCl may also be replaced by HBr or deuterated halide gas for the two reactions. The two reactions provide a new source for $^1O_2$ production, in which the starting materials required are commercially available, moderately priced and safe to handle. The new reactions are attractive for chemical oxygen–iodine laser (COIL).[5,6] Also, they may be used as an alternative source of $^1O_2$ for organic synthesis[7] and waste water treatment.[8]

Also, the KO_2 may be used as a replacement of Na_2O_2 and react with HCl or Cl_2 for $^1O_2$ production which would follow a different balanced equation:

$$2KO_2(s) + 2HCl(g) \rightarrow 2KCl(s) + H_2O(g) + 3/2O_2(^1\Delta_g) \quad (3)$$

$$2KO_2(s) + Cl_2(g) \rightarrow 2KCl(s) + 2O_2(^1\Delta_g) \quad (4)$$

Compared to the reaction (1) or (2), the reaction (3) or (4) can produce an equivalent $^1O_2$ with a much less quantity of the gas reactant which suggests that the reaction can further reduce the weight and cost for $^1O_2$ production as used in COIL system and other applications required $^1O_2$. Alfano and Christe[5a] had studied the reaction of KO_2 with HCl, but a weak emission signal due to $^1O_2$ was observed. They suggested that KO_2 was inferior to alkali metal and alkaline-earth metal peroxides for $^1O_2$ production as reacting with HCl. However, there are no studies undertaken on the $^1O_2$ production from the reaction of KO_2 with Cl_2. In the present study, the $^1O_2$ production from the reaction of solid KO_2 particles with Cl_2 gas was examined and studied.

The gas–solid reactions for $^1O_2$ production were all strongly exothermic chemical reactions which would liberate a large IR blackbody emission and significantly influenced the detection of $^1O_2$ emission when these reactions were conducted in a fixed-bed reactors.[5c,9] The liquid CCl_4 is a favored medium for $^1O_2$ experiments because of the long life time of $^1O_2$ in this solvent (31 ms),[10] and at the same time it can function as a cooling agent and keep a lower temperature of surroundings that would reduce the large IR blackbody emission in the experiments. Therefore, for a convenience in studying and monitoring the $^1O_2$ emission, we developed a reaction system in which the finely divided particles of KO_2 were suspended in liquid CCl_4 by constant stirring in a reaction cell and then react with a continuous flow of Cl_2 gas through the reaction cell (denoted as $KO_2(CCl_4)$–Cl_2).

The emission spectra in the region of 530–805 and 1215–1325 nm from the $KO_2(CCl_4)$–Cl_2 reaction were simultaneously recorded and shown in Figure 1. A strong monomol emission band at 1270 nm due to $O_2(^1\Delta_g) \rightarrow O_2(^3\sum_g{}^-)$[11] and a weak dimole emission bands at 634 or 703 nm due to $2O_2(^1\Delta_g) \rightarrow 2O_2(^3\sum_g{}^-)$[12] were observed. And a relatively stronger emission of $^1O_2$ not only at 1270 nm but also at 634 or 703 nm was observed at the reaction pressure of 700 Torr compared to those at the reaction pressure of 230 Torr. It implied that a higher reaction pressure was favored for $^1O_2$ production in the $KO_2(CCl_4)$–Cl_2 reaction process. It has been reported that the $^1O_2$ may be produced from the reaction of CCl_4 with KO_2,[2] but there are some studies reporting that CCl_4 was inert to KO_2 and could not produce $^1O_2$.[3] Herein, we monitored the emission spectra in the mixing process of KO_2 with CCl_4 in our experiment conditions. Consequently, no any emission band due to $^1O_2$ was observed. The results led us to conclude that the CCl_4 is nearly inert to KO_2 and the most of $^1O_2$ produced from the $KO_2(CCl_4)$–Cl_2 reaction system was generated from the reaction of Cl_2 with solid KO_2 particles.

The chemiluminescence (CL) intensity of $^1O_2$ at 1270 nm was also monitored during the $KO_2(CCl_4)$–Cl_2 reaction course and a sharp and strong CL with duration of ca. 10 s were observed (Figure 2, curve A). When the CL faded away, a

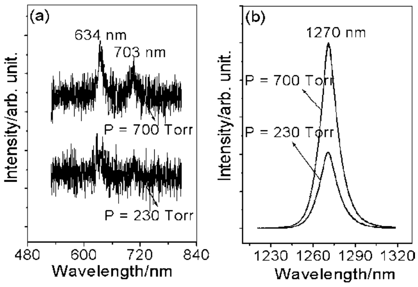

Figure 1. Emission spectra in the region of 530–805 nm (a) and 1215–1325 nm (b) of $^1O_2$ generated from the reaction of Cl_2 with KO_2 (2 g) suspension in CCl_4 (60 mL) at reaction pressure of 230 and 700 Torr.

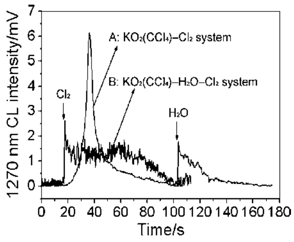

Figure 2. Chemiluminescence (CL) of $^1O_2$ at 1270 nm from: (A) the $KO_2(CCl_4)$–Cl_2 system in which Cl_2 react with KO_2 (10 g) suspension in CCl_4 (60 mL) and (B) the $KO_2(CCl_4)$–H_2O–Cl_2 system in which Cl_2 and H_2O (20 mL) react with KO_2 (10 g) suspended in CCl_4 (40 mL). The reaction pressure of the two reaction systems were all kept at about 700 Torr.

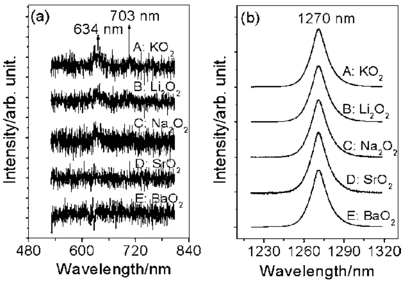

Figure 3. Emission spectra in the region of 530–805 nm (a) and 1215–1325 nm (b) of $^1O_2$ generated from the reaction of Cl_2 gas with different solid reactant suspension in CCl_4 (60 mL): (A) KO_2 (2 g), (B) Li_2O_2 (2 g), (C) Na_2O_2 (6 g), (D) SrO_2 (8 g), and (E) BaO_2 (8 g). The reaction pressure of the five reaction systems was all kept at about 200–230 Torr.

10 mL of H_2O was injected into the reaction cell and a relative weak CL was observed again with duration of ca. 15 s. The results implied that the O_2^- in the surface of solid KO_2 particles could be readily oxidized by Cl_2 and converted to $^1O_2$. However, a layer of solid product of KCl was formed on the solid KO_2 particles. This solid layer of KCl would cause a difficulty in Cl_2 diffusing into the inner of KO_2 particles and reacting with KO_2 and also cause a difficulty in $^1O_2$ rapidly diffusing out of the inside of solid KO_2 particles.

For a comparison, a three-phase reaction of the gaseous Cl_2 and liquid H_2O simultaneously with the KO_2 suspension in CCl_4 (denoted as $KO_2(CCl_4)$–H_2O–Cl_2) was conducted. A relative flatten and a relative weak CL at 1270 nm was observed but with a longer duration of ca. 60 s was observed (Figure 2, curve B). The recorded emission spectra from the $KO_2(CCl_4)$–H_2O–Cl_2 reaction confirmed that the CL at 1270 nm was due to the $^1O_2$ emission (emission spectra see Supporting Information).[14] The results indicated that H_2O could accelerate the $^1O_2$ production from the reaction of Cl_2 with KO_2 and make a complete conversion of KO_2 to $^1O_2$.

The emission spectra from the $KO_2(CCl_4)$–H_2O–Cl_2 reaction was compared to those from the reaction of Cl_2 with the solution of KO_2 dissolved in H_2O and the well-known reaction of Cl_2 with basic hydrogen peroxide (BHP) solution (see Supporting Information).[14] The results indicated that, in the process of the $KO_2(CCl_4)$–H_2O–Cl_2 reaction, the H_2O may dissolve the product of KCl and react with KO_2 and then form a much more reactive specie of HO_2^- which is also presented in BHP solution and can react with Cl_2 with a nearly 100% yield of $^1O_2$.[3b,13] It implied that a nearly 100% yield of $^1O_2$ may be obtained in the $KO_2(CCl_4)$–H_2O–Cl_2 reaction. However, the H_2O increased the $^1O_2$ deactivation in the $KO_2(CCl_4)$–H_2O–Cl_2 reaction process, and we could observe that its maximum of CL intensity at 1270 nm (2.5 mV) was much smaller than the maximum of CL intensity at 1270 nm (6.2 mV) in the $KO_2(CCl_4)$–Cl_2 reaction course (see Figure 2). A rough comparison of their stationary concentration of $^1O_2$ showed the maximum stationary concentration of $^1O_2$ obtained during the $KO_2(CCl_4)$–Cl_2 reaction course may reach nearly a half of that obtained during the $KO_2(CCl_4)$–H_2O–Cl_2 reaction course (see Supporting Information).[14] It implied that $^1O_2$ could also be produced with a high yield from the reaction of Cl_2 with the clean surface of KO_2 particles.

The experiments using the alkali metal peroxides (such as Li_2O_2 and Na_2O_2) or alkaline-earth metal peroxides (such as SrO_2 and BaO_2) as a replacement of KO_2 in the $KO_2(CCl_4)$–Cl_2 reaction were also conducted. A comparison of their emission spectra was shown in Figure 3. Their emission spectra all showed a strong emission band at 1270 nm. But a weak emission band at 634 or 703 nm was only obtained in the reaction system using KO_2 and Li_2O_2 and Na_2O_2 as solid reactant and no emission at 634 or 703 nm was obtained in the reaction system using SrO_2 and BaO_2 as solid reactant. This implied that the KO_2 had the same ability as the alkali metal peroxides and was prior to the alkaline-earth metal peroxides for $^1O_2$ production in efficiency as them reacting with Cl_2.

In summary, $^1O_2$ can be high efficiently produced in the reaction of Cl_2 with KO_2, but it only took place on the surface layer of solid KO_2 particles. The H_2O may accelerate $^1O_2$ production from the reaction of Cl_2 with KO_2 and make a complete conversion of KO_2 to $^1O_2$. And the KO_2 had a similar efficiency for $^1O_2$ production as the alkali metal peroxides (such as Li_2O_2 and Na_2O_2) as reacting with Cl_2, whereas the reaction of Cl_2 with KO_2 was much more economical in weight and cost because it could produce an equivalent $^1O_2$ with a consumption of a half quantity of Cl_2 compared to the reaction of Cl_2 with solid peroxides.

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14 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.