Final Report

SYNTHESIS OF CALCIUM SUPEROXIDE

By: R. T. REWICK, W. G. BLUCHER, and P. L. ESTACIO

Prepared for:

NASA-AMES RESEARCH CENTER
MOFFETT FIELD, CALIFORNIA 94035
Attention: DR. THEODORE WYDEVEN
BIOTECHNOLOGY DIVISION

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INTRODUCTION AND BACKGROUND

Interest in air revitalization systems has recently increased due to the large number of current or proposed research programs that require men to live and work for extended periods in environments completely isolated from our natural atmosphere: space stations, undersea laboratories, defense and pollution shelters, hyperbaric medical chambers, and others. Space and weight requirements often limit the use of compressed air tanks for these applications. Hence, recent emphasis has been on studies of chemicals or chemical systems capable of generating on demand a life-supporting atmosphere. Among the proposed and actually operating systems to supply oxygen are those using alkali and alkaline earth metal superoxides, which possess the capability of releasing O_2 on contact with H_2O.

Of the known metallic superoxides, KO_2 is the least expensive and has been used for many years as the active chemical in the self-contained breathing apparatus used for fire-fighting and mine rescue work. However, canisters containing KO_2 have shown inefficient utilization of the superoxide charge. The inefficiency of such systems can be attributed to the formation of a slurry-type layer of KOH, which prevents further reaction of fresh KO_2 with H_2O. This problem provides considerable impetus to the development of high-purity calcium superoxide. Calcium hydroxide has a much higher fusion temperature than the alkali metal hydroxides and therefore may not form a barrier preventing diffusion of H_2O around the unreacted superoxide. In addition, high purity calcium superoxide has a more favorable O_2 release and CO_2 absorption capacity per unit weight than sodium and potassium superoxides.

Numerous attempts have been made to synthesize pure calcium superoxide. The general approach has involved the reaction between H_2O_2 and calcium peroxide or hydroxide.[1-4] This method generates solid oxide mixtures containing as much as 60% calcium superoxide. To date, methods for consistently producing calcium superoxide of high purity have not been developed.

Previous studies have indicated that at -80°C the oxides of barium, calcium, and magnesium develop a coloration when treated with an O_3/O_2 mixture containing 8% O_3.[5] This observation and the liberation of I_2 when the products were treated with KI solution[6] were given as evidence for the formation of ozonides. Recent experiments involving the ozonation of the oxides of barium, calcium, and magnesium have not revealed a noticeable formation of compounds differing from starting materials.[7,8] However, reactions of calcium oxide, peroxide, and hydroxide with 100% O_3 have not been described and could lead to the formation of the superoxide or ozonide. The formation of calcium ozonide would be significant since it should decompose with heat to the superoxide

$$CaO + 5/3\ O_3 \rightarrow Ca(O_3)_2$$
$$Ca(O_3)_2 \xrightarrow{\Delta} Ca(O_2)_2 + O_2$$

Experimental evidence has shown that oxygen atoms in the first excited state, $O(^1D)$, are a more reactive species than ground state oxygen atoms $O(^3P)$. Possessing the electronic configuration of an empty orbital, $O(^1D)$ atoms have the properties of a very strong acid and are capable of reaction with very weak bases at low temperature and activation energy. At 2537 Å, the quantum yield of $O(^1D)$ atoms generated by photolysis of O_3 approaches unity.

Reaction of $O(^1D)$ atoms generally fall under two categories:

(1) Insertion type[9,10]

$$O(^1D) + CH_4 \rightarrow CH_3OH$$
$$O(^1D) + H_2O \rightarrow H_2O_2$$

(2) Acid-base type[11,12]

$$O(^1D) + N_2 \rightarrow N_2O$$

$$O(^1D) + CO_2 \rightarrow CO_3$$

Experimental evidence further suggests that if $O(^1D)$ and $O(^3P)$ atoms can react with the same substrate to give the same products, the reaction rate will be considerably higher for $O(^1D)$, provided there is appreciable activation energy for the reaction, or if the reaction is endothermic for (O^3P).[13]

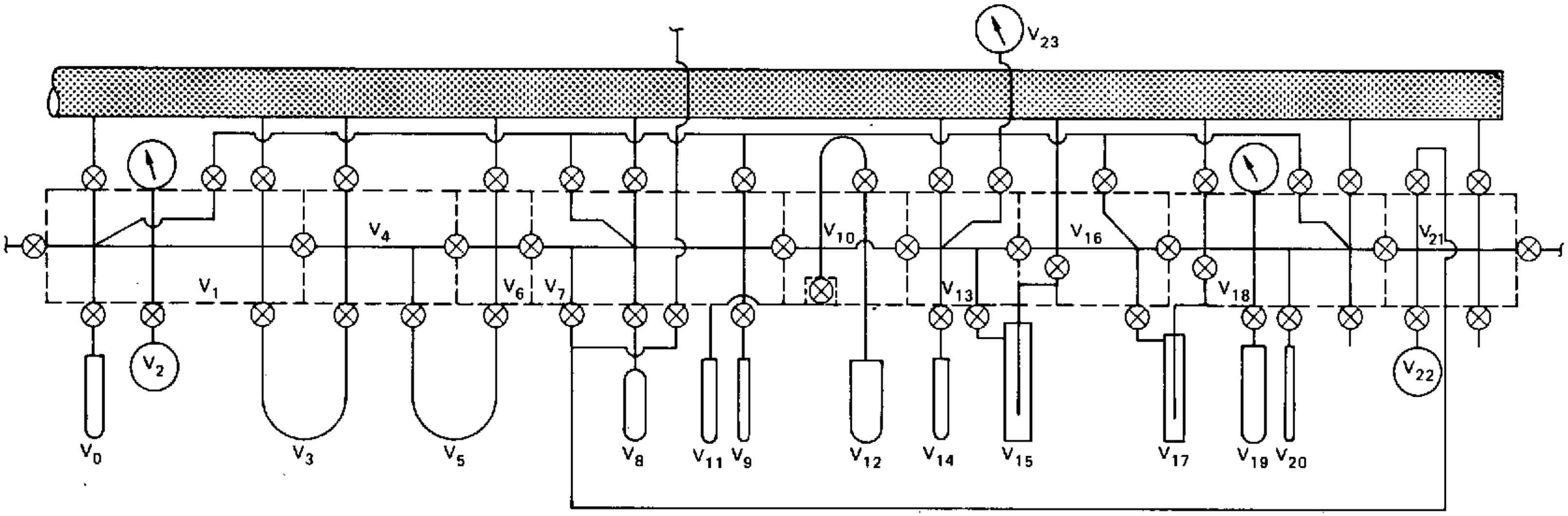
Previous studies have indicated that ground state oxygen atoms $O(^3P)$ are effective in a high yield conversion of KOH to KO_2 (80% purity),[14,15] and a low yield conversion of $Ca(OH)_2$ to $Ca(O_2)_2$ (2.2% purity).[15] The work reported here describes efforts to prepare $Ca(O_2)_2$ from reactions of $Ca(OH)_2$, CaO, and CaO_2 with 100% O_3 and with $O(^1D)$ atoms generated by photolysis of O_3 at 2537 Å.

EXPERIMENTAL

Equipment--The basic apparatus consists of a Monel vacuum line which contains an ozone generator, an ozone storage system, and a flow or static photolysis system for the reaction of calcium oxide, peroxide, and hydroxide with ozone or oxygen atoms. Various parts of the apparatus are constructed from glass and Kel-F. A schematic drawing of the vacuum system is shown in Figure 1; all valves can be operated remotely behind a plexiglass shield. The ozonizer, shown schematically in Figure 2, is constructed from Pyrex glass. A measured quantity of oxygen, condensed into the ozonizer at liquid nitrogen temperature, can be converted to 1 g of 100% O_3 in about 1-1/2 hr by applying a 13.2-kV potential across the 4-mm electrode gap of the ozonizer at -196°C. The ozonizer can also be used to convert a portion of flowing oxygen into ozone. The generated ozone can then be used directly or stored in a silica gel trap V_5 at -78.5°C or in the storage vessel V_8 at -196°C until it is needed. Measured quantities of ozone and other gases can be mixed in the mixing vessel V_{11} and then transferred to the reaction vessel V_{12}.

The reaction vessel V_{12} is a removable 50-cc quartz or Pyrex test tube containing a magnetic stirring bar for static experiments or a 3-cc quartz u-tube for flow experiments. The reaction vessel is surrounded by a Dewar flask to maintain the reaction at a given temperature. For low temperature studies, slush baths were chosen which were transparent to 2537 Å radiation. For reactions at -196°C, a remote temperature controller provides additional N_2 to maintain the temperature. Elevated temperatures were obtained by passing a stream of hot air into the Dewar surrounding the reaction vessel.

The uv source, which surrounds the Dewar, is a Hanovia 10-W helical quartz low pressure mercury lamp built to our specifications.



1. Oxygen purification system – V_0, V_1
2. Ozonizer – V_3
3. Silica gel trap – V_5
4. Storage vessels – V_8, V_{14}, V_{19}, V_{20}, V_{22}
5. Kel-F burette – V_9
6. Mixing vessel – V_{11}
7. Reactor – V_{12}
8. Fractionation traps – V_{15}, V_{17}
9. O-2 atm. Wallace and Tiernan gauge – V_{23}

TB-7846-1R

FIGURE 1 PHOTOLYSIS SYSTEM

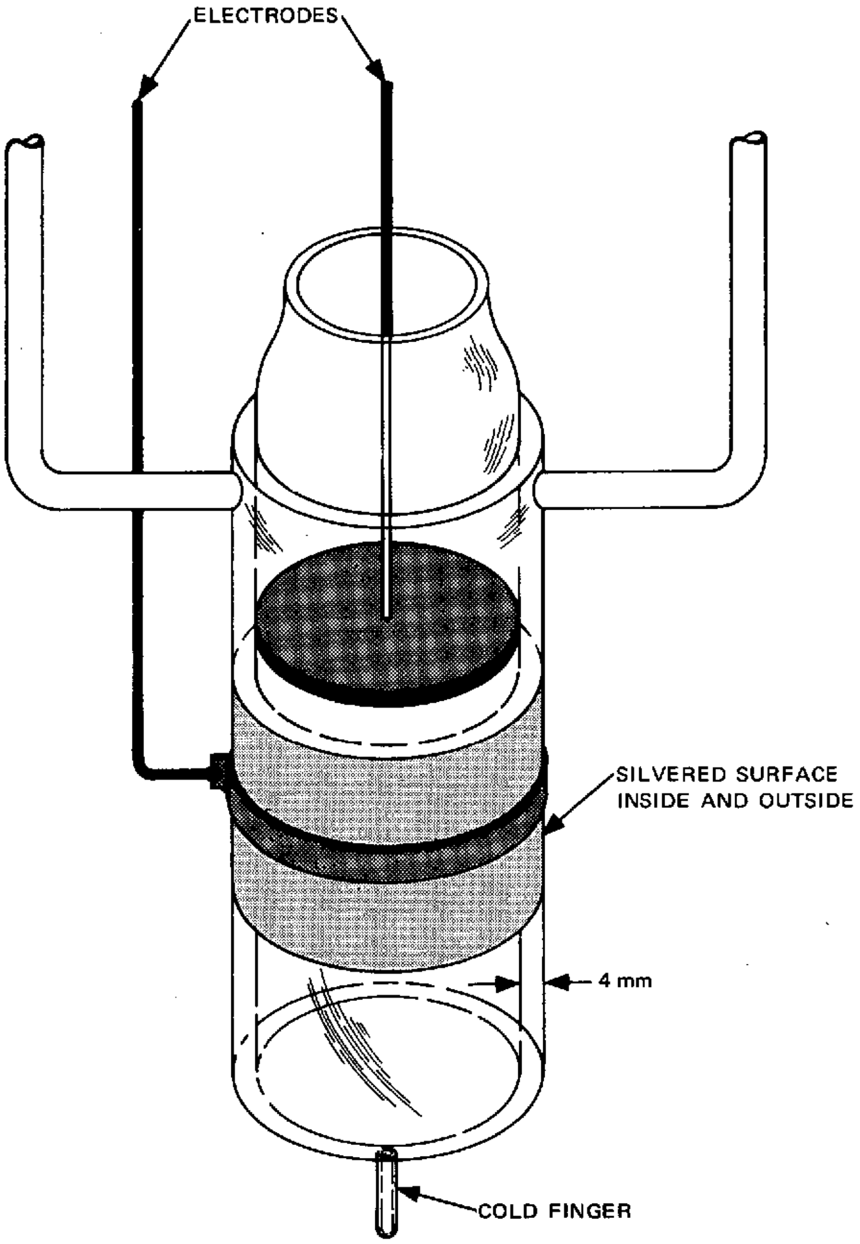


FIGURE 2 OZONIZER

In operation, this lamp generates a sharply defined line spectrum of short wavelength, of which 96.5% is emitted at the resonance line of mercury at 2537 Å. Approximately 2% of the total uv energy may be emitted at 1849 Å. The balance of the uv emission is a scattering of weak lines between 2200 and 4000 Å. Visible and ir radiations are of relatively low intensity.

Materials--Calcium oxide and hydroxide were obtained in their highest commercial purity from Mallinckrodt Chemical Works and used after drying for several hours at 125°C without further purification. Before use, the dried materials were stored in a dry box. Optical grade calcium oxide and 60% calcium peroxide, obtained from Research Organic/Inorganic Chemical Co., and other chemicals used during additive studies were similarly treated. Infrared and emission spectrographic analyses of calcium oxide and peroxide detected the presence of impurities. Ultrapure grade potassium hydroxide was obtained from Alfa Inorganics Co. and purified calcium metal turnings from J. T. Baker Chemical Co. Samples of Potassium superoxide were obtained from Mine Safety Appliance Co. Oxygen, Liquid Carbonic Co. medical grade, 99.5% purity, was further purified by passing the gas over copper oxide turnings heated to 500°C. Ozone (~100% purity) prepared statically was not analyzed other than to measure its vapor pressure at -196°C. Ozone/oxygen mixtures prepared under flow conditions were analyzed by passing the mixture through a neutral buffered potassium iodide solution followed by a standard thiosulfate titration.

Procedure--In general, experiments conducted under static conditions with and without uv irradiation involved reactions of excess O_3 with 100-mg samples of $Ca(OH)_2$ (1.35 mmole), CaO (1.78 mmole), 60% CaO_2 (0.83 mmole), and mixtures containing additives. The dried starting material was transferred in a dry box to the reaction vessel which was then attached to the vacuum line. Gaseous ozone under various conditions was then allowed to contact the solid phase. To improve contact of the material with O_3, some experiments were conducted with a stirred O_3/O_2 solution at -196°C. Visual examination of the starting material during reaction provided a qualitative evaluation of the degree of conversion of the solid phase, since ozonides and superoxides are highly colored species. In cases where a colored product was formed, the solid was analyzed by measuring the oxygen evolved during thermal decomposition or hydrolysis.[16]

Experiments conducted under flow conditions with and without the aid of uv irradiation involved reactions of excess O_3 in an O_3/O_2 gas stream with 100-mg samples of $Ca(OH)_2$ (1.35 mmole), CaO (1.78 mmole), 60% CaO_2 (0.83 mmole), and mixtures containing additives. In the dry box, the dried starting material was loosely packed in the u-tube reactor between quartz wool plugs. After attaching the reactor to the vacuum line, purified O_2 at a pressure of 114 mm Hg and a flow rate of about 30 cc/min was passed through the ozonizer cooled to -78.5°C. The gas stream containing O_3 was then passed through the u-tube reactor maintained at various temperatures. The rate of O_3 production under these conditions, measured in a blank run, was 0.01 mmole O_3/min. Products formed under flow conditions were analyzed as previously described.

RESULTS AND DISCUSSION

A summary of static nonphotolytic experiments with O_3 and $Ca(OH)_2$, CaO, CaO_2 KOH, and Na_2O_2 is presented in Table 1. To improve contact of the solid phase with O_3 and to increase the lifetime of O_3, some experiments were conducted at -196°C with a stirred O_3/O_2 liquid phase. During the course of some experiments with 100% O_3 (g) and CaO, CaO_2, and Na_2O_2, explosions occurred; in more stable systems, the starting materials were allowed to remain in contact with the gas phase for 3 hours. No effort was made to determine the extent of O_3 decomposition; primary emphasis was placed on visual detection of a colored solid phase reaction product. Previous experience with dilute KO_2 samples suggests that concentrations of less than 5 wt% superoxide can be qualitatively detected in this manner. Visual examination of $Ca(OH)_2$, CaO, and CaO containing a small quantity of KOH after treatment with excess O_3 suggested that no reaction to form $Ca(O_2)_2$ had occurred. However, in two experiments with neat CaO_2 at -78.5 and -196°C, a yellow product was formed. After removing unreacted O_3 at -78.5°C, the temperature of the solid was slowly increased. Above -45°C the yellow product began to decompose and within several minutes the solid closely resembled the starting material. The reaction between KOH and 0.5 atm 100% O_3 generated an orange-colored solid, presumed to be KO_3.

A summary of static photolytic experiments with O_3 and $Ca(OH)_2$, CaO_2, CaO, and KO_2 is presented in Table 2. Since O_3 is rapidly decomposed at room temperature by radiation at 2537 Å, its lifetime was considerably increased under photolysis with a liquid O_3/O_2 phase at -196°C. The rate of O_3 decomposition, and hence the rate of $O(^1D)$ production, was further decreased by placing a metal screen around the reactor which reduced the surface area exposed to radiation by about 50%.

Table 1

SUMMARY OF STATIC NONPHOTOLYTIC EXPERIMENTS

	0.25 atm O_3 (g)			0.5 atm O_3 (g)			1.0 atm O_3 (g)			O_3/O_2 (l)
Sample	25°C	0°C	-78.5°C	25°C	0°C	-78.5°C	25°C	0°C	-78.5°C	-196°C
$Ca(OH)_2$ [a]	NR	-	NR	NR	-	-	NR	-	NR	NR
CaO_2 (60%) [a]	Expl	NR	NR	-	NR	-	-	NR	Yellow solid [d]	Yellow solid [d]
CaO [a]	NR	-	-	-	NR	NR	Expl	NR	NR	NR
0.5% KOH [b]	NR	-	-	NR	-	-	-	-	-	-
CaO [a] + 1.0% KOH [b]	-	-	-	NR	-	-	-	-	-	-
5.0% KOH [b]	-	-	-	NR	-	-	-	-	-	-
KOH [a]	-	-	-	Orange solid [c]	-	-	-	-	-	-
KOH [b]	-	-	-	Orange solid [c]	-	-	-	-	-	-
Na_2O_2 (97.4%) [a]	-	-	NR	-	-	NR	-	-	Expl	-

[a] Dried reagent grade

[b] Dried ultrapure grade

[c] Decomposed on standing

[d] Decomposed on warming above -45°C

Table 2

SUMMARY OF STATIC PHOTOLYTIC EXPERIMENTS

Sample	O_3/O_2 (l) -196°C	1 atm O_3(g) 25°C	No O_3 25°C
$Ca(OH)_2$	Yellow solid[c]	NR	
60% CaO_2	Yellow solid[c]	-	
CaO[a]	Yellow solid[c]	-	
CaO[b]	NR	-	
KO_2	-	NR	NR

[a] Reagent grade

[b] Optical grade

[c] Decomposed on warming above -45°C

The screen also served as a protection shield for the Dewar and Hg vapor lamp surrounding the reactor.

When samples of $Ca(OH)_2$, CaO_2, and reagent grade CaO were stirred for 1 hour under photolysis in the presence of excess O_3 in an O_3/O_2 liquid phase at -196°C, a yellow product was formed. After removing unreacted O_3 and O_2 at-78.5°C, the temperature of the reactor was slowly increased. Above -45°C, the yellow product began to decompose, and within several minutes the solid closely resembled the starting material. In a second experiment, the product from the reaction between O_3 and reagent grade CaO was allowed to warm above -45°C into an evacuated bulb. Qualitative mass spectral analysis of the contents of the bulb detected the presence of O_2. Products from the reaction of $Ca(OH)_2$ and CaO_2 with O_3 at -196° were not similarly analyzed. Blank runs with CaO, $Ca(OH)_2$, and CaO_2 under identical conditions with O_2 but no O_3 failed to generate a colored product.

In contrast to the reaction observed for reagent grade CaO with O_3 at -196°C, no colored product was formed with optical grade CaO. To help explain the difference in reactivity between reagent and optical grade CaO to form a colored product during photolysis with O_3, these solids and 60% CaO_2 were analyzed for impurities by infrared and emission spectrographic analysis. Anions detected in the three samples by ir analysis included OH^-, NO_2^-, CO_3^{2-}, and PO_4^{3-}. Sulfides are also impurities commonly found in alkaline earth metal oxides. Although it was difficult to estimate the absolute quantity of each impurity present, optical grade CaO appeared to be considerably less contaminated. The results from emission spectrographic analysis are given in Table 3. Reagent grade CaO appears to be more heavily contaminated with Mg, Y, Ti, Cr, Fe, Al, and Si than does optical grade CaO. The impurity level is even greater with 60% CaO_2.

Table 3

SEMIQUANTITATIVE SPECTROGRAPHIC ANALYSIS

(The following are reported as oxides of the elements indicated.)

	CaO[a]	CaO[b]	CaO_2[c]
Ca	Principal metallic constituent in each		
Na	0.000	0.000	0.3
Mg	0.003	0.4	0.6
Sr	0.06	0.035	0.05
Ba	0.001	-	0.002
Y	-	0.003	-
Ti	-	0.002	0.025
Cr	-	0.001	0.001
Fe	0.003	0.025	0.35
Cu	< 0.001	< 0.001	< 0.001
Al	0.002	0.06	0.400
Si	< 0.01	0.3	0.75
Sn	-	-	0.002

[a] Optical Grade
[b] Reagent Grade
[c] Reagent Grade (60%)

To evaluate the role which these impurities might exhibit in converting reagent grade, but not optical grade, CaO to the colored product, doped samples of optical grade CaO were treated with O_3. In five experiments, samples of optical grade CaO containing 10 wt% $CaCO_3$, ZnS, K_3PO_4, $NaNO_2$, and $Ca(OH)_2$ were photolyzed for 3 hours at 2537 Å in the presence of a liquid O_3/O_2 phase at -196°C. In each case, no coloration of the solid phase was observed. Samples of optical grade CaO were then similarly doped with 10 wt% MgO, Fe_2O_3, TiO_2, and Al_2O_3 and treated as above. Again, in each case, no coloration of the solid phase was observed. Apparently, the major cause of difference in reactivity between reagent and optical grade CaO to form a yellow reaction product with O_3 is not related to the impurity level but may be a function of particle size or crystal structure differences.

A sample of 90% KO_2, analyzed by a gas evolution method,[16] was irradiated for several hours at room temperature and in the presence of an O_3/O_2 liquid phase at -196°C. No gas was evolved during photolysis of the neat solid and no color change observed after the low temperature study. These results suggest that under these conditions KO_2, and perhaps other superoxides, are stable to 2537 Å irradiation.

A summary of nonphotolytic experiments conducted in an O_3/O_2 gas stream with $Ca(OH)_2$, CaO, CaO_2, Ca metal, and KO_2 is presented in Table 4. Visual examination of CaO, $Ca(OH)_2$, and Ca metal samples after treatment for 1 hr with excess O_3 in a flow of O_2 suggested that no reaction to form $Ca(O_2)_2$ had occurred.

Samples of KO_2 and KOH were treated for 1 hour at room temperature and -183°C, respectively, with excess O_3 in an O_3/O_2 gas stream. No color change was observed in the reaction of KO_2 with O_3; a thermally unstable orange solid, presumed to be KO_3, was formed with KOH. Reaction of excess O_3 in an O_3/O_2 gas stream with mixtures of CaO + 10 wt %

Table 4

SUMMARY OF NONPHOTOLYTIC FLOW EXPERIMENTS

Reactant	Temperature, °C -112	 25	 80
CaO^a, $Ca(OH)_2$, Ca^b	NR	NR	NR
CaO_2	Yellow solid[c]	NR	NR
KO_2	-	NR	-

[a] Reagent and optical grade
[b] Powder
[c] Decomposed on warming above -45°C

KOH, CaO + 5 wt % KO_2, $Ca(OH)_2$ + 5 wt % KOH, $Ca(OH)_2$ + 5 wt % KO_2, CaO_2 + 1 wt % KOH, and CaO_2 + 10 wt % KO_2 at -183, 25, and 80°C gave negative or inconclusive results. Apparently these additives exhibit no positive effect in converting CaO, $Ca(OH)_2$, and CaO_2 to $Ca(O_2)_2$.

However, when a sample of CaO_2 was treated for 15 minutes at -112°C with excess O_3 in an O_3/O_2 gas stream, a yellow product was generated. After removing unreacted O_3 and O_2 at -78.5°C, the temperature was slowly increased. Above -45°C the product began to decompose and within several minutes the solid closely resembled the starting material. In a second experiment, the yellow product was allowed to warm above -45°C into an evacuated volume-calibrated bulb. Under these conditions, only a trace of evolved gas was detected. The decomposed product was analyzed for oxygen content by hydrolysis with 0.1 N $KMnO_4$ in a manner similar to that reported by Seyb and Kleinberg.[16] The results are presented in Table 5. Analysis of 90% KO_2 for active O_2 content by $KMnO_4$ and the $FeCl_3/HCl$ solution used by Seyb and Kleinberg[16] gave nearly identical results. The advantage of the $KMnO_4$ method is that for samples containing $CO_3^{=}$ only a trace amount of CO_2 is liberated with O_2.

A summary of photolytic experiments conducted in an O_3/O_2 gas stream with $Ca(OH)_2$, CaO, CaO_2, and Ca metal is presented in Table 6. Visual examination of CaO, $Ca(OH)_2$, and Ca metal samples after irradiation at 2537 Å for 1 hour with excess O_3 in an O_3/O_2 gas stream suggested that no reaction to form $Ca(O_2)_2$ had occurred.

A sample of KO_2 was photolyzed for 1 hour at 80°C under similar conditions in the absence and presence of O_3. No change in color of the starting material was observed in the absence of O_3; with O_3 the color of the solid phase changed from yellow to orange. These results suggest that KO_2 is stable to uv irradiation at 2537 Å, but reacts at 80°C to form KO_3 with $O(^1D)$ atoms generated by photolysis of O_3.

Table 5

ANALYSIS OF $CaO_2 + O_3$ REACTION PRODUCT

	O_2 Evolved (STP), mmole/gm		%CaO_2
Product	During Color Change	After Color Change ($KMnO_4$)	After Color Change
~ 60% CaO_2	0	3.97	57.2
$CaO_2 + O_3$	Trace	4.07	58.7
$CaO_2 + O_3$ (uv)	0.18	4.82	69.5

Table 6

SUMMARY OF PHOTOLYTIC FLOW EXPERIMENTS

	Temperature, °C		
Reactant	-112	25	80
CaO[a] $Ca(OH)_2$, Ca[b]	NR	NR	NR
CaO_2	Yellow solid[c]		
KO_2	-	-	Orange solid

[a] Reagent and optical grade

[b] Powder

[c] Decomposed on warming above -45°C

When a sample of CaO_2 was photolyzed for 30 minutes with excess O_3 in an O_3/O_2 gas stream, a yellow product was formed. The conversion of the starting material to the colored product appeared to be greater than in previous reactions, based on the intensity of the coloration. After removing unreacted O_3 and O_2 at $-78.5^\circ C$, the temperature of the solid was slowly increased. Above $-45^\circ C$, the yellow coloration began to fade and within several minutes the solid closely resembled the starting material. In a second experiment, the yellow product was allowed to warm above $-45^\circ C$ into an evacuated volume-calibrated bulb. Under these conditions, a measured quantity of gas was collected, which, by mass spectral analysis, was found to be O_2. The decomposed solid product was then analyzed for active oxygen content by hydrolysis[16] with 0.1 N $KMnO_4$. A sample from the nonphotolyzed reaction between CaO_2 and O_3 was treated in a similar manner.

The results from these studies, compared to untreated CaO_2, are given in Table 5. The results clearly show that treatment of 57.2% CaO_2 with O_3 increases the active oxygen content of the sample; the effect is further enhanced by photolysis. If the formation and decomposition of the yellow product can be represented by

$$\mathrm{CaO_2} + 2\ \mathrm{O} \underset{> -45^\circ\mathrm{C}}{\overset{\mathrm{uv},\ -112^\circ\mathrm{C}}{\rightleftharpoons}} \mathrm{Ca(O_2)_2}$$

then gas measurement results suggest the formation of additional CaO_2 by reaction of O_3 with starting material impurities.

Since pure CaO_2 was not available for a comparative study, it is difficult to predict that CaO_2 is the major reactant to form the colored product although similar reactions of CaO and $Ca(OH)_2$--the suspected major impurities--with O_3 failed to generate a colored product. The reaction products from these studies were not analyzed for increase in active oxygen content.

Since $Ca(O_2)_2$, prepared from the decomposition of $CaO_2 \cdot 2H_2O_2$, is reported to be stable up to 50°C in mixtures containing 40 wt % $Ca(O_2)_2$[3], the thermal decomposition observed here is probably complex and may involve oxidation of an impurity, thereby releasing only a portion of the available superoxide oxygen.

Further consideration should be given to the possibility that the colored product formed is $Ca(O_3)_2$, although most known metal ozonides are orange-red in color.[17] The thermal decomposition of hypothetical $Ca(O_3)_2$ may not yield $Ca(O_2)_2$ as expected, but may proceed further to form CaO_2.

Therefore, a calculation of the superoxide content of the product could be in error if the identity of the product and its decomposition mechanism are not known. However, based on the assumption that the quantity of O_2 evolved during the color change is equivalent to the amount of $Ca(O_2)_2$ formed at -112°C, the concentration of $Ca(O_2)_2$ present before decomposition is calculated to be 1.9%.

By increasing the reaction time of O_3 with CaO_2, the O_3 concentration, or changing the geometry of the reaction zone, it is likely that a higher conversion to the colored product can be acheived. In additon, the use of purer CaO_2 will help to define the role impurities may play in the formation or decomposition of the product.

SUMMARY

The work reported here describes efforts to prepare $Ca(O_2)_2$ from reactions of calcium compounds with 100% O_3 and with $O(^1D)$ atoms generated by photolysis of O_3 at 2537 Å. Samples of $Ca(OH)_2$, CaO, CaO_2, Ca metal, and mixtures containing suspected impurities to promote reaction have been treated with excess O_3 under static and flow conditions in the presence and absence of uv irradiation. Studies with KO_2 suggest that the superoxide anion is stable to radiation at 2537 Å but reacts with oxygen atoms generated by the photolysis of O_3 to form KO_3. Calcium superoxide is expected to behave in an analogous manner.

With 100% gaseous O_3 under some conditions, samples of CaO and CaO_2 initiated rapid gas phase decomposition (explosion). Under more controlled conditions at -196°C, treatment of these solids and $Ca(OH)_2$ with a photolyzed O_3/O_2 liquid phase resulted in the formation of a solid having the typical yellow coloration of a superoxide. However, the solid formed under these conditions was not stable above -45°C; in the case of the CaO reaction product, O_2 was evolved as the color change from yellow to white occurred above this temperature.

Similar results were obtained at -112°C for CaO_2 when the solid was treated with excess O_3 in an O_3/O_2 gas stream. The coloration of the reaction product was enhanced by photolysis of the gas stream. As the colored products decomposed above -45°C, samples of evolved O_2 were collected and measured. The decomposed solid samples were then analyzed by hydrolysis for active oxygen content, and the results compared with untreated CaO_2. The data show that treatment of CaO_2 with O_3 at -112°C is effective in increasing the active oxygen content of the sample; a marked increase is observed with uv irradiation. Although the coloration of the product formed in the reaction between

O_3 and CaO_2 strongly suggests the presence of $Ca(O_2)_2$, the reason is not clear for the decomposition of the product above -45°C. Based on the assumption that the quantity of O_2 evolved during the color change is equivalent to the amount of $Ca(O_2)_2$ formed at -112°C, the concentration of $Ca(O_2)_2$ present before decomposition is calculated to be 1.9%.

By increasing the reaction time of O_3 with CaO_2, the O_3 concentration, or changing the geometry of the reaction zone, it is likely that a higher conversion to the colored product can be achieved. In addition, the use of purer CaO_2 will help to define the role impurities may play in the formation or decomposition of the product.

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