Practical Synthesis of Dichlorine Monoxide[†]

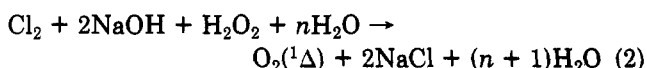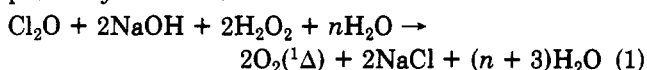**John H. Hain, Jr., and Henry A. McGee, Jr.***

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A continuous reaction scheme and apparatus were designed and developed to synthesize Cl_2O for use in the generation of $O_2(^1\Delta)$ from H_2O_2 for subsequent use in pumping the I atom laser at 1.315 μm. Chlorine was reacted with anhydrous Na_2CO_3 in a fixed or fluidized bed reactor at 180 °C. The product gases were collected in CCl_4 or in KI solution and analyzed by an iodometric titration technique. Cl_2 conversion was 89%.

Introduction

The chemical laser is nothing more than a flow reactor in which the product is coherent radiation rather than some chemical species. All of the usual design problems of fluid flow with simultaneous reaction and diffusion are evident.

Dichlorine monoxide (Cl_2O) may be useful for the generation of $O_2(^1\Delta)$ for subsequent use in the Chemical Oxygen Iodine Laser (COIL). This highly unusual laser uses only "off the shelf" reagents to react directly to produce high power beams (McDermott et al., 1977). COIL systems as large as 10 kW cw have been operated using Cl_2. Dichlorine monoxide may be contrasted with Cl_2 which is presently used in COIL

$$Cl_2O + 2NaOH + 2H_2O_2 + nH_2O \rightarrow$$
$$2O_2(^1\Delta) + 2NaCl + (n + 3)H_2O \quad (1)$$

$$Cl_2 + 2NaOH + H_2O_2 + nH_2O \rightarrow$$
$$O_2(^1\Delta) + 2NaCl + (n + 1)H_2O \quad (2)$$

A mole of Cl_2O may double the conversion of peroxide to $O_2(^1\Delta)$ as compared to present technology using Cl_2. Both reactions are diffusion controlled; gaseous Cl_2O or Cl_2 must diffuse into liquid peroxide to react, and the $O_2(^1\Delta)$ must then diffuse back into the gas phase and be pumped into the laser cavity before it degrades to the ground state ($^3\Sigma$). With its dipole moment of 0.78 D, we expect Cl_2O to diffuse into H_2O_2/H_2O more rapidly than does Cl_2. Dichlorine monoxide is five times more soluble in water than is Cl_2, and hopefully this greater solubility will be evident in peroxide as well. From all these perspectives, a greater production rate of $O_2(^1\Delta)$ was anticipated.

Singlet delta oxygen readily transfers its energy to monatomic iodine through a series of steps that are not well understood (Heidner et al., 1981). In multiple collisions, $O_2(^1\Delta)$ dissociates I_2 and produces $I(^2P_{1/2})$. The energy mismatch between $O_2(^1\Delta)$ and $I(^2P_{1/2})$ is only 279 cm^{-1}, so the exchange is efficient. When iodine is stimulated to return to its ground state, $I(^2P_{1/2}) \rightarrow I(^2P_{3/2})$, a photon is emitted at 1.315 μm, which constitutes the laser action (McDermott et al., 1977).

The purpose of this research was to ultimately replace Cl_2 with Cl_2O in COIL by developing a practical production process that would be continuous, efficient, inexpensive, and easy to operate.

Experimental Section

Fluidized beds for gas/solid reactions are common in large-scale chemistry, but they are almost unknown in

laboratory scale work. This absence need not be so, as is evident from the technique developed here to synthesize Cl_2O.

In the 150 year history of Cl_2O, synthetic procedures involving either mercuric oxide or sodium carbonate have been most attractive (Renard and Bolker, 1976). Mercuric oxide is hazardous, and its cost demands regeneration with attendant complexities. The carbonate process

$$2Cl_2 + Na_2CO_3 \rightarrow Cl_2O + CO_2 + 2NaCl \quad (3)$$
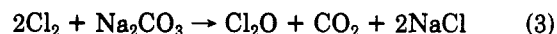
requiring temperatures of 150 to 200 °C, was selected (Renard and Bolker, 1976). Anhydrous Na_2CO_3 is reacted with Cl_2 in a column 75 mm i.d. × 1 m in height. The bed of Na_2CO_3 was supported by a 1.6 mm thick stainless steel fritted plate, which distributed the entering gas (Cl_2 to N_2 ratio of about 1 to 2 to moderate the reaction) uniformly over the cross section of the reactor. The bed was intermittently fluidized with N_2 to abrade away the salt layer that forms on the surface of the solid particles. It was then returned to a fixed bed to react with chlorine once more. This cycling or pulsed-fluidization procedure could be repeated or timed as desired, including continuous fluid-bed reaction if downstream processing can handle the required gas flows. In the apparatus described here, intermittent fluidization was more convenient. The product gases exiting the reactor were sparged into a sample collector, which was designed to efficiently handle 500 mL of solution. Dichlorine monoxide can also be collected as a liquid by cooling the collector to –78 °C (Dangerous!) Unreacted Cl_2 may subsequently be removed from the Cl_2O by simple distillation by pumping at –78 °C. Although the vapor pressure of Cl_2 is about 13 times that of Cl_2O at –78 °C, some Cl_2 will be lost. This distillation is dangerous since liquid Cl_2O is shock sensitive and can explode. For operation in the laser, it may not be necessary to condense the Cl_2, but rather it may be used immediately in the peroxide reactor to make $O_2(^1\Delta)$.

The reactor column and collector were made of Pyrex, and 1.5 kg of Na_2CO_3 produced a quiescent bed 30 cm deep. Chlorine and N_2 entered through stainless steel or monel tubing and fittings. Heating tape controlled by a Variac maintained the temperature of the column, which was also wrapped with glass wool. Column temperature also increased due to the exothermic reaction.

The Na_2CO_3 was initially heated to about 180 °C, while N_2 passed through the bed at 105 mL/s (STP) to ensure that the sodium carbonate was anhydrous. During startup, gases were vented from the bottom of the column, which allowed adjustment to the desired flow rates. Timing started and ended when bubbles were observed and ceased in the sample collector. During fluidization of the bed, the sample collector valve was closed simultaneously with opening the vent valve at the top of the reactor. A

timing cycle of 5 to 15 min fixed-bed followed by 2 min fluidized bed was convenient. This particular cycle was arbitrarily selected, even though the time to cover an Na_2CO_3 particle with NaCl could be calculated sufficiently for design purposes. During the fluidization mode, the N_2 flow rate was 180 mL/s (25 °C, 1 atm). The minimum experimental fluidization rate was 60 mL/s, which is a function of particle size, particle geometry, solid density, fluid viscosity, and fluid density. Gases from the reactor were bubbled through a fine frit into KI solutions or into CCl_4 held at 5 °C to prevent evaporation of the liquids due to entry of the hot product gases.

Samples were analyzed immediately by an iodometric titration technique. Dichlorine monoxide and chlorine react with iodide ion to form iodine

$$Cl_2O + 4I^- + H_2O \rightarrow 2OH^- + 2Cl^- + 2I_2 \qquad (4)$$

$$Cl_2 + 2I^- \rightarrow 2Cl^- + I_2 \qquad (5)$$
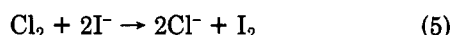
Conditions must be neutral to acidic to titrate iodine with sodium thiosulfate; therefore, a known amount of acid was added to ensure that the hydroxide ion from Cl_2O was neutralized. After the first titration, the residual acid was determined by first adding a slight excess of potassium iodate, which liberated additional iodine that was then titrated

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + H_2O \qquad (6)$$
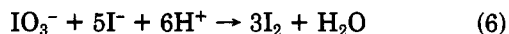
The first titration determined the amount of Cl_2O and Cl_2, while the back-titration determined the amount of Cl_2O alone. Carbon tetrachloride as an indicator (red-violet to colorless) was far superior to soluble starch, especially when titrating Cl_2O in the presence of Cl_2. Starch can form a water-insoluble complex with iodine, which causes a drift in the end point.

The $Cl_2O/Cl_2/CCl_4$ solution was analyzed both by the above titration technique and by mass spectroscopy, but the latter was unsuccessful because of the high reactivity of Cl_2O (Freeman and Phillips, 1968). Instrumental techniques are best conducted in line. Upon adding anhydrous acetic acid to CCl_4 solutions, if Cl_2O is present, water is formed which then floats on the surface. This is a convenient qualitative test for Cl_2O.

Results

The results and operating parameters are listed in Table I. The agreement between the timed entering mass of Cl_2 (rotameter) and the exiting mass of Cl_2 (titration) was always within experimental error. The major sources of error arose from the rotameter calibration, OH^- ions neutralized by CO_2 co-product in the water, and the volatility of Cl_2O over CCl_4. The titration data were corrected for this latter error using a Henry's Law constant of 1830 mmHg at 25 °C (Renard and Bolker, 1976). Henry's law applies best to dilute solutes; the concentration of Cl_2O was 0.279 M, which was likely too concentrated for accu-

Table I. Operating Parameters and Results

	expt			
	I	II	III	control
total reaction time, min	17.5	30.5	215	24
Cl_2 flow rate, (cm³/min) 1 atm, 25 °C	378	42	10	32
N_2 flow rate, (cm³/min) 1 atm, 25 °C	1320	84	20	n/a
average column temp, °C	180	180	180	n/a
fluidized flow rate, (cm³/s) 1 atm, 25 °C	180	180	180	n/a
fixed-bed time per cycle, min	5	5	15	n/a
fluidized bed-time per cycle, min	2	2	2	n/a
average conversion, %	42 ± 1	74 ± 2	89 ± 0.2	0
Cl_2 entering reactor, mol	0.293	0.0572	0.0960	0.0343
Cl_2 exiting reactor, mol of Cl_2, Cl_2O, and NaCl	0.305	0.0583	0.100	0.0344
collecting solution	KI (aq)	KI (aq)	CCl_4	CCl_4

rate use. In a control experiment, Cl_2 was bubbled through CCl_4 and analyzed as above for Cl_2O; no Cl_2O was present.

The kinetics could be inferred as first order. A simple plug-flow model of the reactor

$$(u/L)(dX/dz') = k(1 - X) \qquad (7)$$

suggests that a plot of conversion, X, vs. L/u (contact time) should give an exponential curve if the rate is either first order with respect to Cl_2 or if the reaction is diffusion controlled. Here u is the linear velocity of Cl_2 at the inlet plane of the reactor and z is a dimensionless length given by height in the bed divided by its total height, L. The rate constant, k, can be obtained from the slope and compared with a calculated mass transfer coefficient from standard correlations to suggest whether the reaction is in fact diffusion controlled. The values of L/u for experiments I, II, and III were 26.5, 357, and 1500 s, respectively, but these data alone do not allow an accurate analysis.

The fluid-bed method can be operated continuously at any capacity using either a fast-fluidized bed or the new vibro-fluidized bed both with continuous influx of fresh carbonate and outflow of spent NaCl.

Acknowledgment

Registry No. Cl_2, 7782-50-5; Cl_2O, 7791-21-1; Na_2CO_3, 497-19-8.

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