DTIC FILE COPY

AD-A214 847

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)

2. REPORT DATE 30 June 83

3. REPORT TYPE AND DATES COVERED Final (14 Mav 82- 14 Aug 82

4. TITLE AND SUBTITLE
STUDIES IN SINGLET DELTA OXYGEN IN SUPPORT OF COIL

5. FUNDING NUMBERS
61102F
2303-D9

AUTHOR(S)
Henry A. McGee, Jr

PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Department of Chemistry
Virginia Polytechnic Institute
Blacksburg, VA 24061-6496

8. PERFORMING ORGANIZATION REPORT NUMBER
AFOSR-TR- 89-1396

SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AFOSR
BLDG 410
BAFB DC 20332-6448

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
AFOSR-82-0199

1. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release;
distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

DTIC
S ELECTE D
NOV.28 1989
B

14. SUBJECT TERMS

15. NUMBER OF PAGES 11

16. PRICE CODE

17 SECURITY CLASSIFICATION OF REPORT unclassified

18. SECURITY CLASSIFICATION OF THIS PAGE unclassified

19. SECURITY CLASSIFICATION OF ABSTRACT

20. LIMITATION OF ABSTRACT

NSN 7540-01-280-5500

Standard Form 298 (890104 Draft)
Prescribed by ANSI Std. 239-18

89 11 27 111

STUDIES ON SINGLET DELTA OXYGEN IN SUPPORT OF COIL

Final Scientific Report

AFOSR-82-0199 (a minigrant)

June 30, 1983

AFOSR.TR. 89-1390

by

Henry A. McGee, Jr.

Professor of Chemical Engineering and Principal Investigator

Contd from pg. 1

Abstract

Peroxide Chlorine Oxide Oxygen

1 Delta

Chlorine

Sodium Carbonate

cc

Although it is a highly reactive and dangerous species, Cl_2O is potentially more than twice as effective in reducing H_2O_2 to $O_2(^1\Delta)$ than is Cl_2. It has been conveniently and routinely synthesized from the reaction of Cl_2 with Na_2CO_3 in a fluidized bed reactor configuration. Conversions are of the order of 80 percent, and a typical rate in our facility of 6 cm^3/sec of Cl_2 yields 0.5 gm/min of Cl_2O. The now convenient production, handling, and analysis of Cl_2O was preliminary to our study of its efficacy in producing $O_2(^1\Delta)$.

1 Delta

Keywords: Chemical Oxygen Iodine Laser

INTRODUCTION

In significant measure, COIL is an exercise in chemical engineering. The traditional chemical engineering concerns of chemical reaction with simultaneous heat, mass, and momentum transport processes are evident in the optical cavity as well as in the upstream manufacture of $O_2(^1\Delta)$. The ultimate product of COIL is coherent radiation while much more usually, the chemical engineer is concerned with the production of some chemical compound, say penicillin, as a product. But the scientific issues are very similar. This Laboratory is concerned with all of the chemistry of COIL:

a) the production of Cl_2O

b) the efficacy of Cl_2O in the production of $O_2(^1\Delta)$

c) the energy transfer from $O_2(^1\Delta)$ to I to produce
 an inversion of highest possible number density.

This specific project was concerned only with the first of these interests, that is, with the design, construction, and operation of a reaction and purification facility for the routine production of Cl_2O.[1]

The goal is ultimately a more efficient and more compact COIL. At the present time, $O_2(^1\Delta)$ is produced from basic peroxide by the reaction

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

whereas the reduction of peroxide with Cl_2O proceeds similarly

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

but wherein we see that one mole of chlorine oxide will produce <u>two</u> moles of $O_2(^1\Delta)$ rather than one as is produced with chlorine itself. In addition to that, Cl_2O is five times more soluble in water than is Cl_2, and we anticipate a correspondingly greater solubility in basic peroxide as well.

Although the chemistry with peroxide is favorable, Cl_2O is a difficult and, in many ways, obnoxious substance. Some of its more fundamental properties are summarized below[2]:

Normal boiling point: 2°C
Freezing point: -120.6°C
Heat of formation: 18.1 ± 0.3 kcal/mol (273.15 K)
Free energy of formation: 21.95 kcal/mol (273.15 K)
Absolute entropy: 63.76 cal/mol K (25°C)
Fundamental absorption frequencies (cm^{-1}) 684, 320, 973
Nonlinear molecule with dipole moment of 1.83 Debyes
Ionization potential: 11.16 ± 0.10 eV
A pale orange-yellow gas that condenses to a reddish-brown liquid

Two general techniques were considered for the preparation of Cl_2O; one involving reaction of chlorine with mercuric oxide and the second involving reaction of chlorine with sodium carbonate and perhaps related species. The mercuric oxide technique has the advantage of a convenient regeneration of HgO from the $HgCl_2$ that is formed in the Cl_2O synthesis reaction. Thus a recycle or regenerative process can be designed. But this process also has the distinct disadvantage of using a highly poisonous powder. We elected to avoid the HgO process for that reason. The sodium carbonate process proceeds as follows,

$$2Cl_2 + 2Na_2CO_3 + H_2O \rightarrow Cl_2O + 2NaHCO_3 + 2NaCl$$

$$2Cl_2 + 2NaHCO_3 \rightarrow Cl_2O + 2CO_2 + 2NaCl$$

This is also the industrial process in use for the production of chlorine oxide.

PROCESS DEVELOPMENT

As is always the case, the development of a convenient and efficient process for the production a relatively unusual chemical has been an evolutionary process. In this Section, we briefly describe the major milestones in this evolutionary process development.

The first design of our production facility is shown schematically in Figure 1. The reactor is a section of 4 in. diameter glass pipe with a 3 ft. tall packed bed of lumps of Na_2CO_3 pentahydrate. The lumps are up to about 0.5 in. in diameter. The tower contains 3 kg. of carbonate. Moisture is removed by passing the product stream through a tower of P_2O_5 containing 0.5 kg. of the drying agent. The Cl_2O and unreacted Cl_2 are condensed in the cold trap that is maintained at any temperature down to -78°. The temperature of the trap is automatically maintained by a refrigerant circulating system using an L&N recorder/controller in a simple on-off control mode. Most of the unreacted Cl_2 will pass through the condensation trap if it is maintained at -60°C. The traces of Cl_2 that do condense to contaminate the Cl_2O product can be removed by pumping on the liquid held at -78°C.

The problem with this particular reactor configuration is the formation of salt (NaCl) which can be seen growing on the surface of the sodium carbonate as the reaction proceeds. Thus the progress of the reaction in effect turns off the reaction. We then developed a fluidized bed process in which the fine particles of Na_2CO_3 are in continuous violent agitation against each other such that the salt that is formed on the surface is abraded away to continuously expose fresh carbonate to the incoming chlorine. The schematic of this second evolution in the process development is very much like that of Figure 1, except now the nitrogen flow rate is very high to maintain the fluidized carbonate bed. The N_2

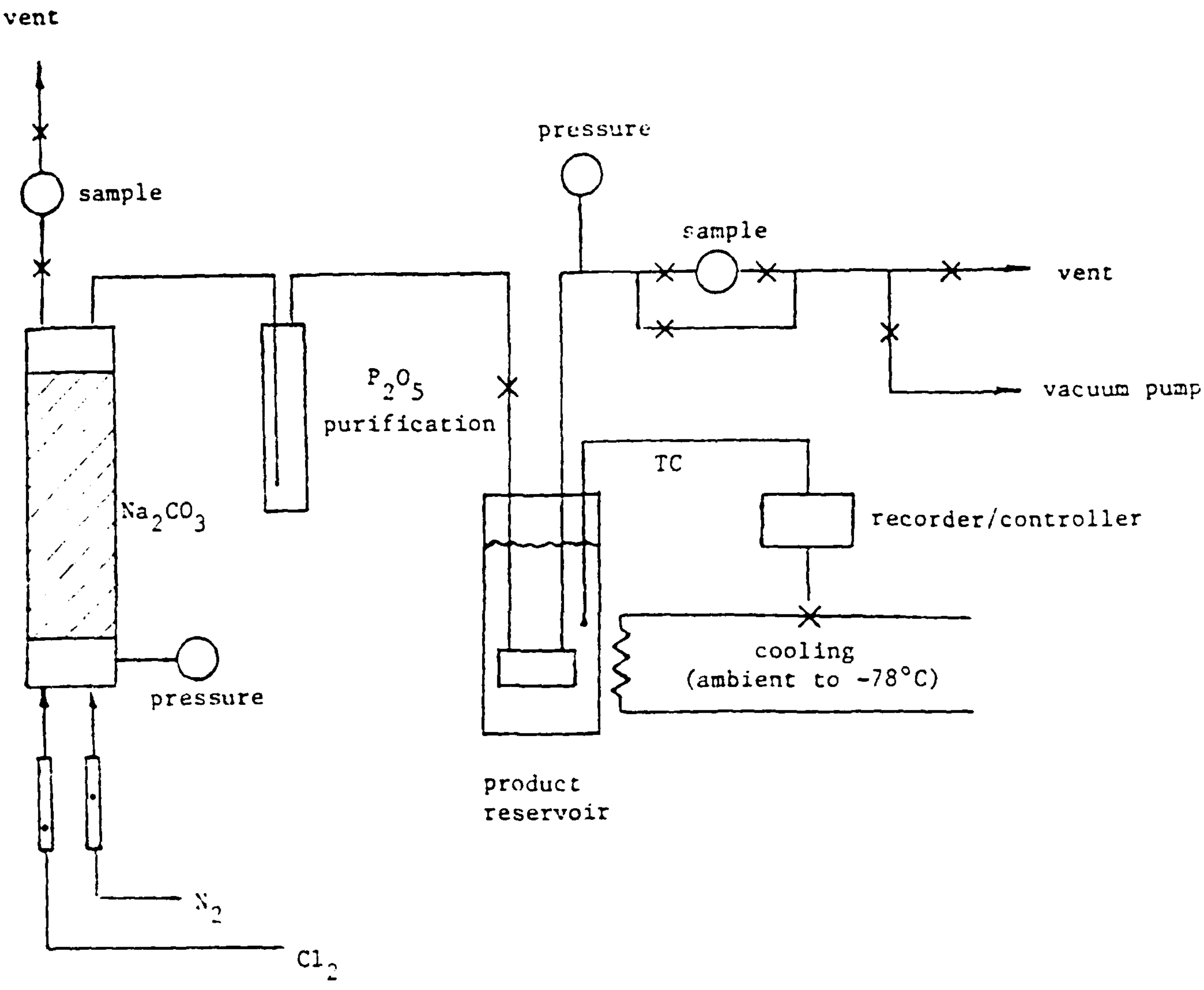

Figure 1: Schematic of facility developed for the production of Cl_2O.

flow is controlled with a stainless steel globe valve and the Cl_2 is controlled with a monel needle valve. The flow rates of both gases are noted using previously calibrated rotameters. The gases are distributed across the cross-section of the bed by a stainless steel frited plate. Approximately 1.5 kg of sodium carbonate provided a one-foot deep quiescent bed of solid. The maximum N_2 flow rate to fluidize the bed was 272 cm^3/sec. The minimum rate was 52 cm^3/sec. In initial experiments, the product reservoir of Figure 1 was replaed by a simple carbon tetrachloride trap which removed all of the incoming Cl_2O and chlorine. Analysis of this solution suggested that the conversion was approximately 80%. The analysis is particularly convenient with the Cl_2O and Cl_2 in CCl_4 solution. Now the product of the titration is water which is insoluble in the CCl_4 and the water then appears as a second phase floating on the CCl_4.

A difficulty with this latter configuration is the high nitrogen flow that is required to maintain the fluid bed. This large amount of gas rushing through the remainder of the flow system is troublesome. Therefore the third and final modification of the original process is that of use of an intermittent fluidized bed. Here the chlorine is admitted through a quiet bed and Cl_2O is formed. The chlorine is then closed off, the downstream system is closed, the reactor is vented, and the bed is fluidized with a heavy stream of nitrogen. This abrades away the salt, exposing fresh carbonate, the bed is then allowed to settle, and the gentle stream of chlorine readmitted. An alternative possibility here would be to merely gently stir the solid bed during the chlorine admission. This too should abrade away the salt.

ANALYSIS

Monitoring of the synthesis process as well as the subsequent purification utilized both our Varian MAT 112 mass spectrometer as well as a conventional iodometric titration. For mass spectrometric analyses, a sample was captured in a 200 ml stainless steel sampling flask for subsequent manipulation. The wet chemical analysis utilized a titrimetric technique in which the Cl_2O reacts with iodide.[3] Either water or carbon tetrachloride was used as a solvent for the Cl_2O product in performing the iodometric analyses. Chlorine monoxide and chlorine liberate iodine from iodide as follows:

$$KI + H_2O \rightarrow K^+ (aq) + I^- (aq) + H_2O$$

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

$$Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$$

A known excess of acid (usually acetic acid) must be added to neutralize the OH^- ion. Iodine in solution has a bright yellow color, so it is easily titrated using sodium thiosulfate by the following reaction:

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

Soluble starch solution was used as an indicator at low iodine concentrations. The blue-violet color that is produced allows for sharp end-point determinations. The presence of the OH^- ion is useful when titrating solutions of both Cl_2O and Cl_2, for a back titration can be performed to determine the amount of residual acid. Excess potassium iodate is added to liberate iodine for the back titration by the following chemistry:

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$

The iodine is again titrated with sodium thiosulfate. Thus, the first titration determines both the amount of Cl_2O and Cl_2, while the back titration determines the amount of chlorine monoxide alone.

Iodometric titrations can also be performed in carbon tetrachloride solutions. There are two benefits in using CCl_4 as a solvent. One benefit is that more concentrated solutions are obtained with CCl_4, since chlorine monoxide is more soluble in CCl_4 than in water. The second benefit is that iodine has a bright violet color in solution with CCl_4, even at low iodine concentrations. Therefore, sharp end-points are obtained without the use of an indicator such as soluble starch. Both iodometric titrations are quantitative.

The chemical test involving anhydrous acetic acid is only qualitative and is only suitable for carbon tetrachloride solutions. The chemistry is illustrated below:

$$Cl_2O + 2AcOH \rightarrow 2AcOCl + H_2O$$

When Cl_2O is present in the CCl_4, an aqueous phase will appear floating on the CCl_4 phase. This "quick and dirty" qualitative test was convenient and frequently used.

PERSONNEL

The process development for the manufacture of Cl_2O has formed the MS thesis of Mr. John Hain. Mr. Hain was educated in Chemistry at the Coast Guard Academy and was a dual major in chemistry and mathematics at SUNY-Albany before joining this Department as a graduate student seeking to develop expertise in chemical engineering built upon his baccalaureate education in pure chemistry. This is a difficult transition, it requires approximately a year of remedial work in the undergraduate core courses in chemical engineering and Mr. Hain has accomplished all of this in good order. A copy of the thesis will be submitted to AFOSR when its preparation is completed in a few weeks.

CONCLUSIONS

The reaction of chlorine with sodium carbonate in a fluidized bed reactor provides an efficient and convenient process for the production of chlorine oxide. In typical laboratory-size preparations, 1.5 kg of sodium carbonate is fluidized in a 4 in. ID glass reactor with nitrogen flowing at 270 cm^3/sec (STP) with a simultaneous injection of chlorine at about 6 cm^3/sec (STP) The reaction operates at room temperature and the conversion to chlorine oxide is approximately 80%.

FUTURE WORK

With the production of chlorine oxide conveniently in hand, we will be exploring now the efficacy of this reagent in producing singlet delta oxygen from peroxide as mentioned in the Introduction. Detection of the oxygen is by monitoring the dimol emmission at 1.27 μm using a liquid nitrogen cooled germanium detector. This detector must be calibrated against an ESR machine, and our calibration is not yet complete. We are presently theoretically examining a number of reactor configurations and designs in an attempt to achieve the optimum balance between gas-liquid contacting on the one hand with removal of a fragile and continuously decomposing product species on the other hand. This is, of course, an old problem in chemical engineering generally as well as in this particular system, and it has been studied by a number of investigators in the recent past.[4,5,6] As initial "proof" experiments with the chlorine oxide we plan to merely duplicate the Rocketdyne reactor[4] which has been shown to be rather efficient. With success there, a new engineering analysis for improved reactor design with Cl_2O will be carried out.

In the final analysis, if COIL is to be more efficient than with present technology, we must produce high number densities of $O_2(^1\Delta)$ and I atoms in the optical cavity. This is also a problem in chemical engineering reactor design which we are also now considering.

REFERENCES

1. This project was conducted under the terms of a minigrant that formed a part of the program for Summer Faculty Research Participants at various Air Force research facilities. The PI was stationed at AFWL during the summer of 1981 and this project ended on 15 November 1982.

2. J. J. Renard and H. I. Bolker, Chem. Rev. 76, 487 (1976). This is an excellent review paper on this unusual species.

3. "Vogel's Textbook of Quantitative Inorganic Analysis," 4th edition, 1978, p. 370.

4. "Engineering Development of a Singlet Delta Oxygen Generator," S. C. Hurlock, Rockwell International, March 1982, AFWL-TR-80-153.

5. "Engineering Development of a Singlet Delta Oxygen Generator," R. J. Richardson, McDonnell Douglas, Feb. 1981, AFWL-TR-80-109.

6. "Engineering Development of a Single Delta Oxygen Generator," P. K. Conn, Bell Aerospace Textron, May 1981, AFWL-TR-80-144.