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Chemical Generator and EPR Studies of the Chemical-Oxygen-Iodine-Laser System

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Formation of $O_2(^1\Delta)$ by reaction of Cl_2 gas with basic H_2O_2 liquid was studied using a small scale batch reactor. Effect on $O_2(^1\Delta)$ yield of certain reaction/reactor parameters were evaluated. Parameters included molarity of base and presence of $Cl^{(-)}$ in initial reaction solution, use of Br_2 as reactant, depth of Cl_2 injector in solution, area of cooled trap surface, and use of halocarbon coating on flow tube walls. Use of Cl_2, base molarity, and trap condition were areas in which greatest effects were

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observed. Mixtures of argon and I_2 were added to the flowing output from the generator and the high-field (1.7-2.4 T) EPR spectrum was scanned. No I_2 or I species were observed. Values of g_{exp} for two previously unreported EPR lines in the J=3 level of $O_2(^1\Delta)$ were obtained.

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TABLE OF CONTENTS

SUMMARY

Formation of $O_2(^1\Delta)$ by reaction of Cl_2 gas with basic H_2O_2 liquid was studied using a small scale batch reactor. Effect on $O_2(^1\Delta)$ yield of certain reaction/reactor parameters were evaluated. Parameters included molarity of base and presence of Cl^- in initial reaction solution, use of Br_2 as reactant, depth of Cl_2 injector in solution, area of cooled trap surface, and use of halocarbon coating on flow tube walls. Use of Cl_2, base molarity, and trap condition were areas in which greatest effects were observed. Mixtures of argon and I_2 were added to the flowing output from the generator and the high-field (1.7-2.4 T) EPR spectrum was scanned. No I_2 or I species were observed. Values of g_{exp} for two previously unreported EPR lines in the J=3 level of $O_2(^1\Delta)$ were obtained.

PREFACE

This is the Final Report on work done in Work Unit 2303-F4-01, Chemiluminescent Gas Phase Reactions. The work reported in Part 1 was accomplished during the period, Feb 1980 to May 1981. During this period and up to Jan 1982, our major research tool, the EPR spectrometer, was not available for use due to a major modification following equipment failure. The work reported in Part 2 was done between Jan 1982 and Aug 1982. We wish to acknowledge the assistance of Lt Col McDermott and Nick Pchelkin at the Air Force Weapoins Lab, both in discussions of our work and in providing financial and material aid, often on short notice. We thank Dr Larry Dalton of the University of Southern California for his assistance during problems in the EPR modification and very helpful discussions. Other individuals who did much to get this project going and keep it going were Capt Lee Myers, Major Mike DeLong, and Sgt Miles Scott. Finally, we gratefully acknowledge the timely and expert assistance of our glassblower, Fred Kibler, and the excellent job of typing the manuscript done by Judy Cross.

LIST OF FIGURES

LIST OF TABLES

Introduction

The chemical generation of $O_2(^1\Delta)$ has received considerable attention[1, 2, 3] as a means of pumping a high energy $O_2(^1\Delta)/I$ atom transfer laser.

The reaction which to date has proven most successful in terms of % $O_2(^1\Delta)$ in the O_2 generated is that of gaseous Cl_2 with concentrated basic H_2O_2 liquid. The overall stoichiometry of the reaction is:

$$Cl_2 + 2OH^- + H_2O_2 \longrightarrow O_2 + 2H_2O + 2\ Cl^-.$$

The reaction is difficult to study in a controlled experiment because it involves rapid transport of gaseous Cl_2 into the liquid phase, followed by rapid reaction and transport of the O_2 formed out of the liquid and into the gas phase. Our previous efforts to study the reaction have involved monitoring various reaction system parameters including output content as the reaction proceeds[4, 5]. While these results provided some useful information, they did not yield direct evidence regarding the actual reaction mechanism or specific sources of deactivation. This final report contains two parts. The first part deals with our attempts to vary certain reaction/reactor parameters of a small scale batch reactor to identify which parameters most affect % $O_2(^1\Delta)$ in the output and thus merit further study. The second part deals with efforts to characterize the output flow from the generator when I_2 is injected into it, and in particular, attempts to observe the electron paramagnetic resonance spectrum of any excited I_2 which may be formed.

Part 1. Parameter Variation in Small Scale Batch Reactor.

I. INTRODUCTION

The approach here was to compare % $O_2(^1\Delta)$ output over a range of output pressures from a small scale batch reactor while keeping all parameters as constant as possible except for the one under consideration. The parameters studied in this way included:

1. Substitution of Br_2 for Cl_2
2. Initial molarity of base (KOH)
3. Added initial concentration of Cl^- (KCl)
4. Depth of Cl_2 injector in basic H_2O_2 solution
5. Area of in-reactor trap surface cooled
6. Effect of halocarbon coating of flow tube on $O_2(^1\Delta)$ deactivation

II. EXPERIMENTAL

A diagram of the experimental system is shown in Fig 1. Matheson high-purity chlorine is bubbled through the basic H_2O_2 solution formed from equal volumes of 90% H_2O_2 and either aqueous KOH or NaOH solution normally at 6M. Total solution volume was normally 200 ml. The solution is poured into the reaction vessel through the port holding the thermometer, which has been removed to bring the system up to ambient pressure. The system is then resealed and pumped down slowly to a pressure of 0.1 to 0.2 torr. In this process, the reaction solution normally cools to about -15°C due to evaporative cooling. When Cl_2 is bubbled through the solution, its temperature rises to about -5°C. The gas output from the solution flows past the in-reactor trap containing an ethanol-dry ice slush to trap H_2O, H_2O_2, and any other gases condensible at -78°C. The gas then flows into the blackened Wood's horn device where the $O_2(^1\Delta)$ 1.27μ emission is detected using a Wang intrinsic germanium solid state detector cooled to 77 K and fitted with a 1.27μ filter.

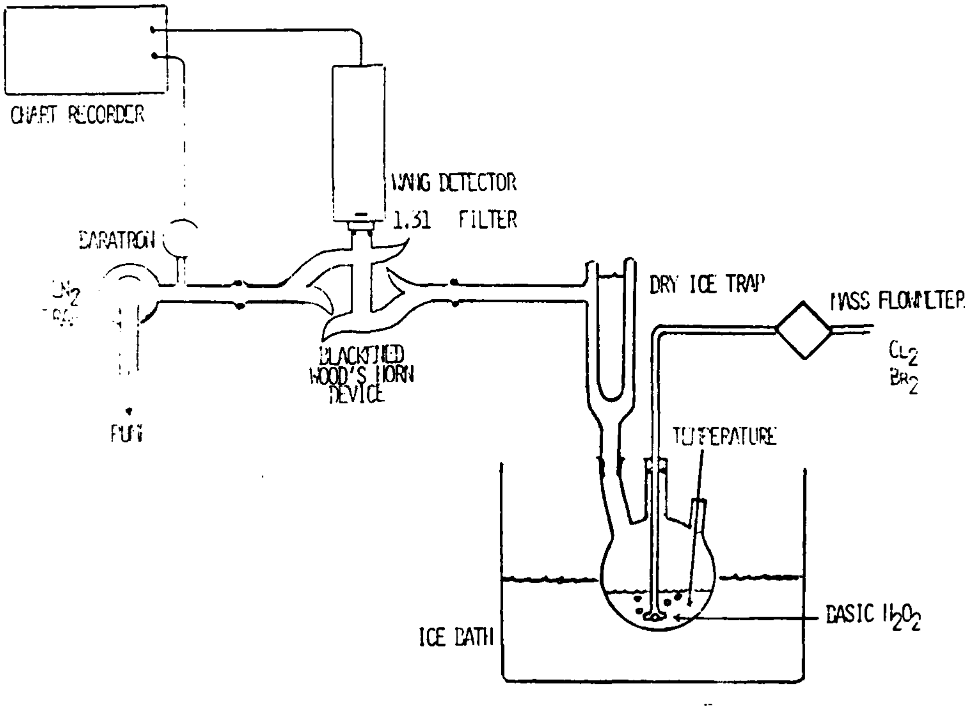

Fig 1. Small scale batch reactor flow apparatus.

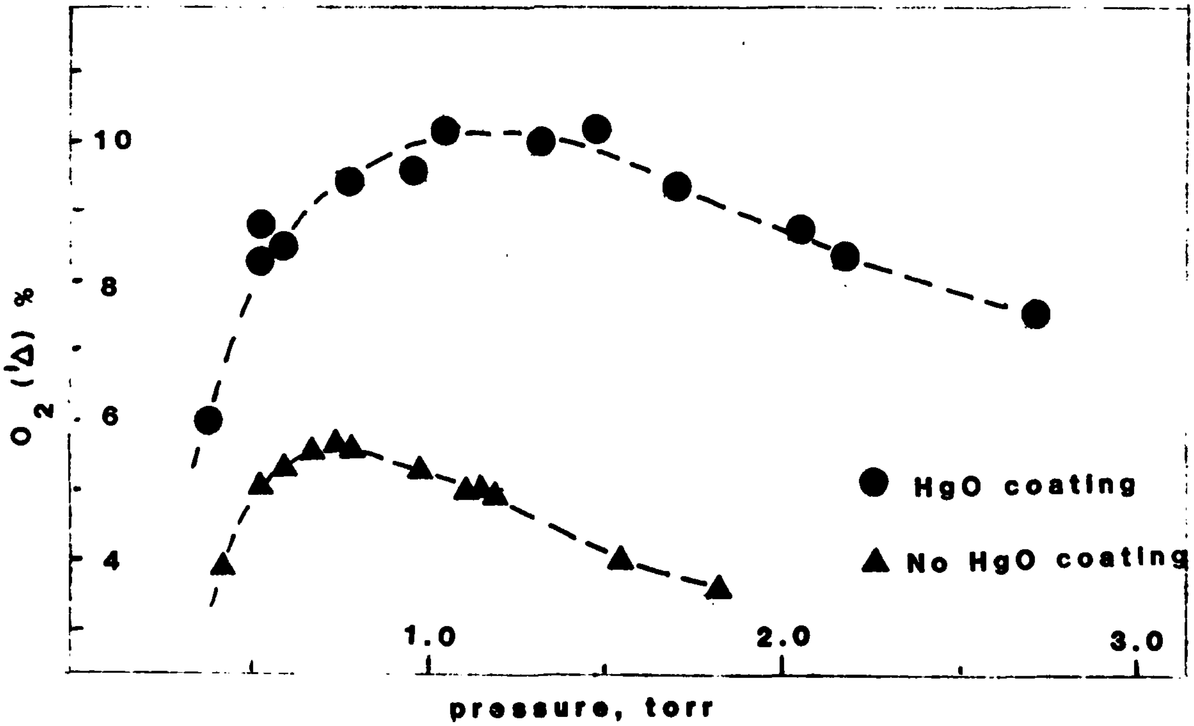

Fig 2. Microwave discharge-generated $O_2(^1\Delta)$ % as a function of O_2 pressure at detector.

The Wang signal was recorded along with pressure detected by a MKS Baratron capacitance manometer on a dual-channel chart recorder. The detection system was calibrated by flowing O_2 through the microwave discharge at various pressures. The O_2 flow tube and microwave cavity were inserted into the system in place of the generator for calibration. The discharge was operated at about 70 watts forward/5 watts reflected power. Under these conditions, the % $O_2(^1\Delta)$ at 0.8 torr total pressure can be assumed to be about 10%[6]. Thus the signal from the Wang can be compared to 10% of the total O_2 pressure to give a conversion factor for Wang signal to $O_2(^1\Delta)$ pressure. Absolute accuracy was not of concern here since the experiments were designed to be comparative. An example of the microwave $O_2(^1\Delta)$ output as a function of pressure in this system is shown in Fig 2. This figure also shows the importance of using a mercuric oxide coating to eliminate oxygen atoms, which are involved in $O_2(^1\Delta)$ deactivation processes, from the flow. Pressures were normally varied by simply changing the molar flow rate of O_2 into the system, and, in the case of chemical generation, changing the molar flow rate of Cl_2 into the generator.

% $O_2(^1\Delta)$ in chemical generation experiments was obtained by assuming that the pressure measured in the detection system was due to O_2 only. Thus any Cl_2 passing through the generator unreacted would tend to lower the calculated % $O_2(^1\Delta)$. Previous work[5] using similar reactor conditions have shown that normally no more than 10% of the reactor output pressure is due to gases other than O_2.

1. <u>Cl_2/Br_2 Comparison</u>. About 100 ml of liquid $Br_{2(l)}$ was placed in a 5 liter round bottom flask with a cold-finger. The Br_2 was frozen in the cold-finger using liquid nitrogen and the flask was evacuated. The Br_2 was then allowed to melt and the process repeated. The flask was then placed into a thermostated bath at 40°C and connected to the line used to feed Cl_2 gas into the reactor. The reactor was then operated as described above.

2. Initial KOH Molarity Variation. Solutions were prepared by adding 100 ml of KOH solutions of varying molarity to 100 ml 90% H_2O_2 cooled to -20°C. The exothermic mixing was controlled to keep the solution temperatures under 20°C. These solutions were then used in runs as described above.

3. Addition of Cl^- to Reaction Solution. Two pairs of runs were performed with solutions made from 50 ml of 6M KOH and 50 ml 90% H_2O_2. In one run of each pair, the initial solution was also made 1.0M in KCl. In one pair of runs, the pressure was varied by controlling Cl_2 flow rate. In the other pair, Cl_2 flow rate was fixed to give a total output pressure of 0.8 ± 0.2 torr and the % $O_2(^1\Delta)$ was followed as a function of time.

4. Depth of Cl_2 Injector in Solution. In this run, the Cl_2 injector was variably positioned from 1 to 10 cm below the surface of the reaction solution. Output pressure was kept constant at 0.8 torr. Flow velocity was varied by adjusting the Cl_2 flow rate and the valve downstream of the detector to maintain the 0.8 torr output pressure.

5. Variation of In-reactor Trap Surface Cooled. In this series of runs the 1.5 cfm pump was replaced by a 15 cfm pump which resulted in higher $O_2(^1\Delta)$ signals at the detector. The reactor used is shown in Fig 3. The surface of the in-reactor trap which is cooled was varied by adjusting the depth of the funnel-insert in the trap. Air was blown into the space between the insert tube and trap wall. This kept the trap wall above the lower end of the insert tube near the temperature of other uncooled surfaces. Under each condition of constant trap surface area cooled, runs were performed in which the Cl_2 flow rate into the reactor and output pressure were kept constant.

6. Effect of Halocarbon Coating on $O_2(^1\Delta)$ Deactivation. The microwave discharge was used to generate O-atom free flows of $O_2(^1\Delta)$ in this experiment. A 60 cm length of a U-shaped flow tube (2.4 cm ID) was inserted into the system between

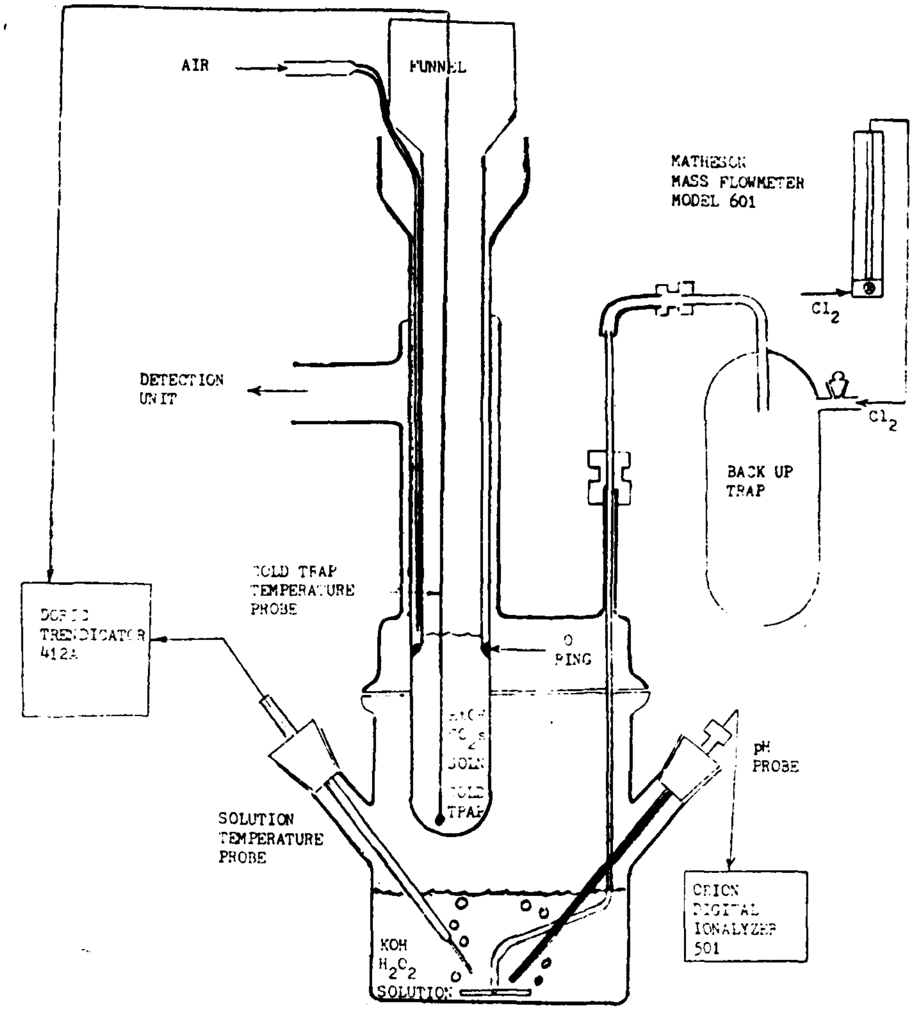

Fig 3. Small-scale generator with variable trapping surface.

the microwave discharge and the Wang detector. Runs were performed with the clean tube and with the tube walls coated with Fluoroglide halocarbon coating. Comparisons were made with two identical tubes at various pressures and at 20°C and -78°C.

III. RESULTS

1. Cl_2/Br_2 Comparison. Several runs with Br_2 were performed in the range 1-2 torr total output pressure and % $O_2(^1\Delta)$ values between 3 and 5% were observed. Thus, the reaction with Br_2 gives % $O_2(^1\Delta)$ values which are 2 to 3 times less than those obtained using Cl_2, for which values of about 12% were obtained under similar conditions. Since the $O_2(^1\Delta)$ %'s are calculated using the assumption that all the output pressure is due to O_2, we cannot determine with certainty whether the lower $O_2(^1\Delta)$ output is due to poorer utilization of Br_2 or other factors involving the reaction/deactivation processes. However the amount of Br_2 collected on the LN_2 trap did not appear to be significantly different from the amounts of Cl_2 observed on the trap when Cl_2 was used.

2. Initial Molarity of Base (KOH). Runs were performed with the initial molarities of KOH at 1.0, 3.0, 6.0, 9.0, and 12.0 M. The results are shown in Fig 4. The run at 9.0 M is not shown since it was essentially the same as the run at 12.0 M. Some of the scatter in these results is due to the fact that pressures were varied randomly so that % $O_2(^1\Delta)$ values at about the same pressure were taken at different times during the run. As has been shown previously[4, 5], % $(^1\Delta)$ decreases during the course of a run in a batch reactor as base is depleted. However, there appears to be no doubt that the optimum KOH molarity in this type of generator is about 6.0 M when mixed in 1:1 volume ratio with 90% H_2O_2.

3. Additional Concentration of Cl^- (KCl). Fig 5 shows the pair of runs performed with constant Cl_2 flow rate. Within experimental error, the two runs are

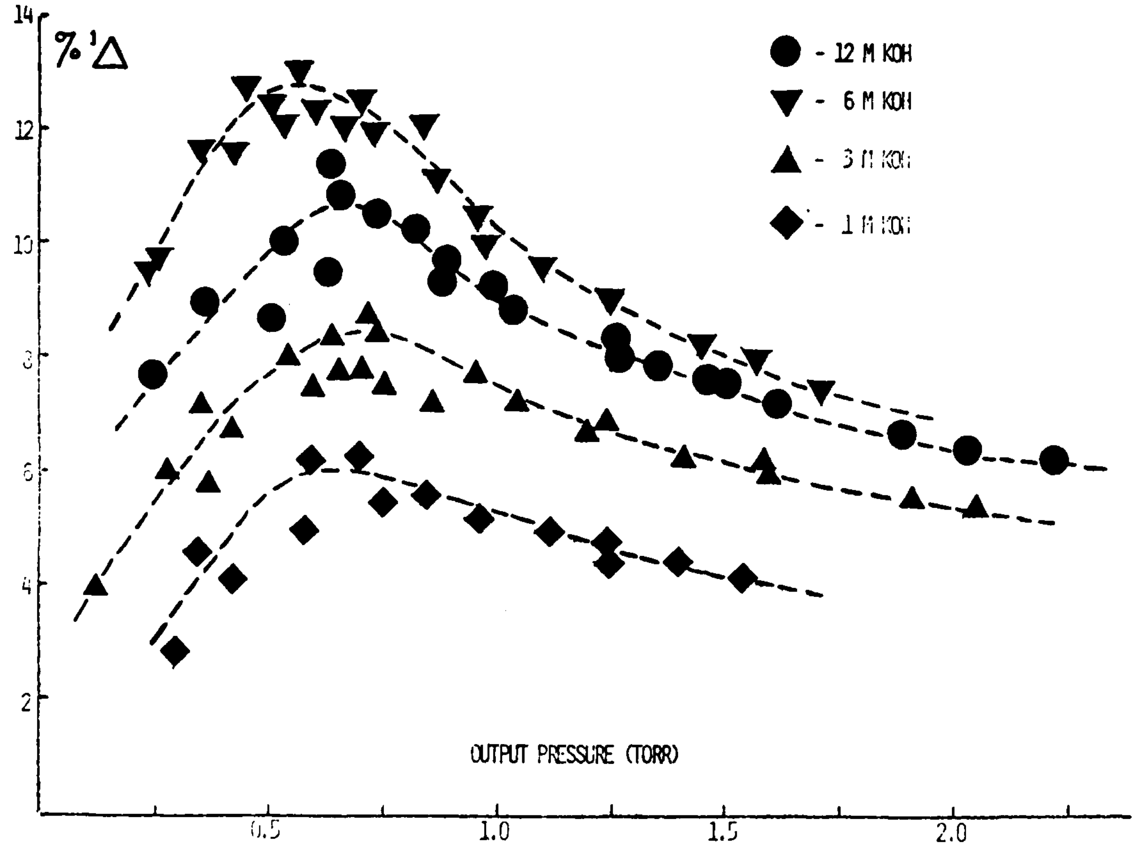

Fig 4. Effect of initial KOH molarity on $O_2(^1\Delta)$ %.

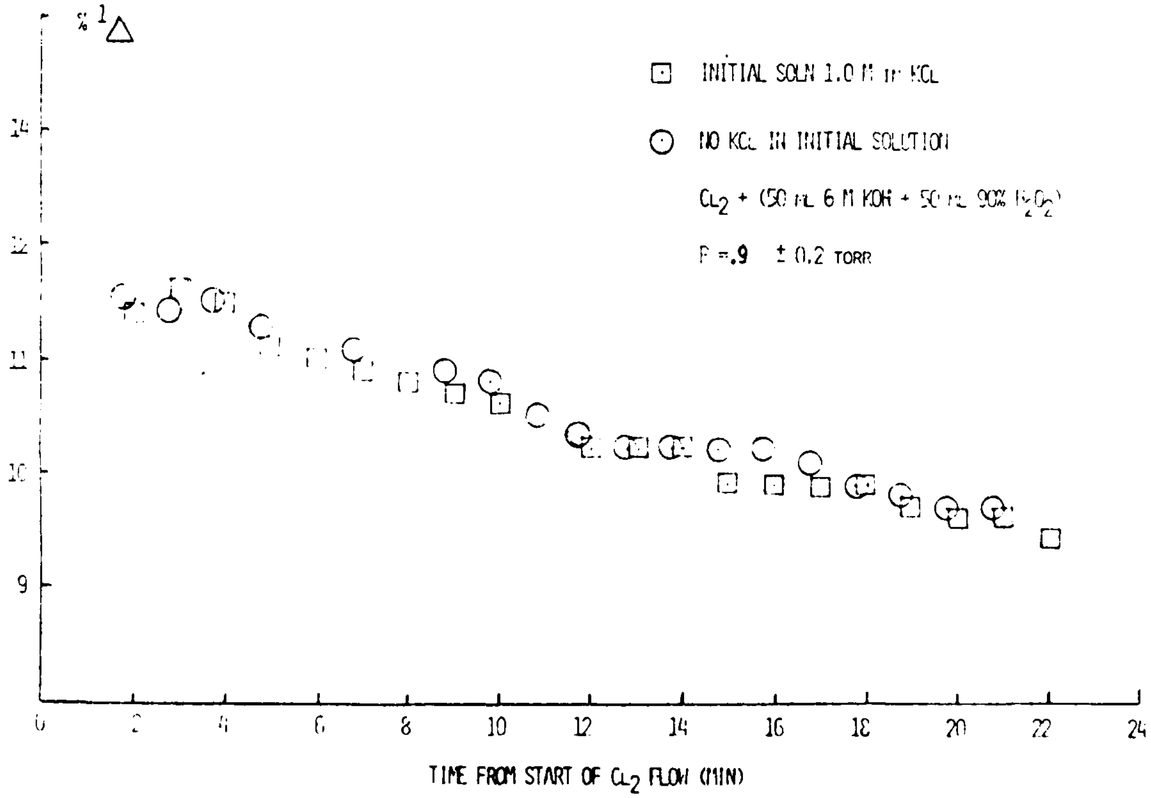

Fig 5. Effect of added Cl^- in initial reaction solution.

identical. The runs in which pressures were varied also showed that additional initial Cl^- (and thus also Cl^- generated during the course of a run) has no apparent effect on the rate of $O_2(^1\Delta)$ production.

4. Depth of Cl_2 Injection in Solution. The $O_2(^1\Delta)$ output from this reactor generally was not a function of the depth of the Cl_2 injector in the solution. Only when the Cl_2 flow rate was reduced to less than 0.01 mmole s^{-1} was there any indication that the % $O_2(^1\Delta)$ decreased when the injector depth was increased from 1 cm to 10 cm below the solution surface.

5. Variation of In-reactor Trap Surface Cooled. This experiment illustrated most clearly how difficult it is to use a batch reactor in parametric studies. Extensive measures would have to be taken to keep all other pertinent reactor parameters constant while varying the cooled trap surface area. As can be seen in Table 1, the change in cooled surface area affected the solution temperature, the background pressure, and probably also the residence time in the reactor because of the change in the cryogenic pumping effect of the trap. Thus, estimates of $O_2(^1\Delta)$ % becomes even more difficult to deduce and compare. However, an attempt to evaluate this trap effect was made using the following rationale. Since we measure the molar flow rate of Cl_2, we can use it as an estimate for the molar flow rate of the O_2 output (since the stoichiometry is 1:1 and utilization is 90-100%). Further, the molar flow rate of the background vapor, which we can assume to be primarily H_2O, can be estimated using the background pressure observed prior to Cl_2 addition. Thus, the partial pressure O_2 in the output can be estimated from the total pressure and the molar flow rate fraction of O_2. The estimated O_2 pressure in the flows in the runs in Table 1 were nearly constant in the range 0.45 - 0.55 torr. The $O_2(^1\Delta)$ signal shown is the average signal obtained over the first 2 minutes of the run, when build-up of condensed material on the trap surface should not be a significant factor. Thus the $O_2(^1\Delta)$ signals observed indicated that higher $O_2(^1\Delta)$ %'s were obtained from the generator when the maximum trap surface was cooled.

Table 1. Variation in Cooled Trap Surface Area

AREA COOLED cm^2	BACKGROUND PRESSURE torr, ± 0.05	TOTAL PRESSURE OF OUTPUT torr, ± 0.05	SOLUTION TEMPERATURE °C	$O_2(^1\Delta)$ SIGNA ARB. UNITS
234	0.1	0.6	-10 to 0	38
146	0.5	0.9	-9 to -5	24
69	1.0	1.5	-5 to 0	23

The occurrence of higher $O_2(^1\Delta)$ %'s with larger surface area cooled was observed in two other series of runs. In these runs, pressures and trap temperatures were not well controlled, so the data is even less amenable to interpretation. However, results of one of these runs are shown in Fig 6. This graph shows the average $O_2(^1\Delta)$ % over the first 10 minutes of each run as a function of the trap area cooled.

6. Effects of Halocarbon Coating on $O_2(^1\Delta)$ Deactivation. Deactivation of $O_2(^1\Delta)$ was not significantly affected by coating the walls of the flow tube inserts with Fluoroglide halocarbon coating. A slight (about 5%) decrease in $O_2(^1\Delta)$ signal was observed in the higher pressure range (1.5 - 3.0 torr, where $O_2(^1\Delta)$ % ranges from 3-5%) when the tubes were cooled to -78°C.

IV. DISCUSSION

The overall goal of the work described in Part I was to determine which aspects of the generator operation affected $O_2(^1\Delta)$ % in the output sufficiently to merit detailed study. The batch reactor used here appeared adequate to address this goal, but showed little promise as a tool for more detailed studies.

The lower $O_2(^1\Delta)$ % generated by the Br_2 and basic H_2O_2 reaction may be due in part to the fact that the reaction of Br^- in aqueous H_2O_2 to yield

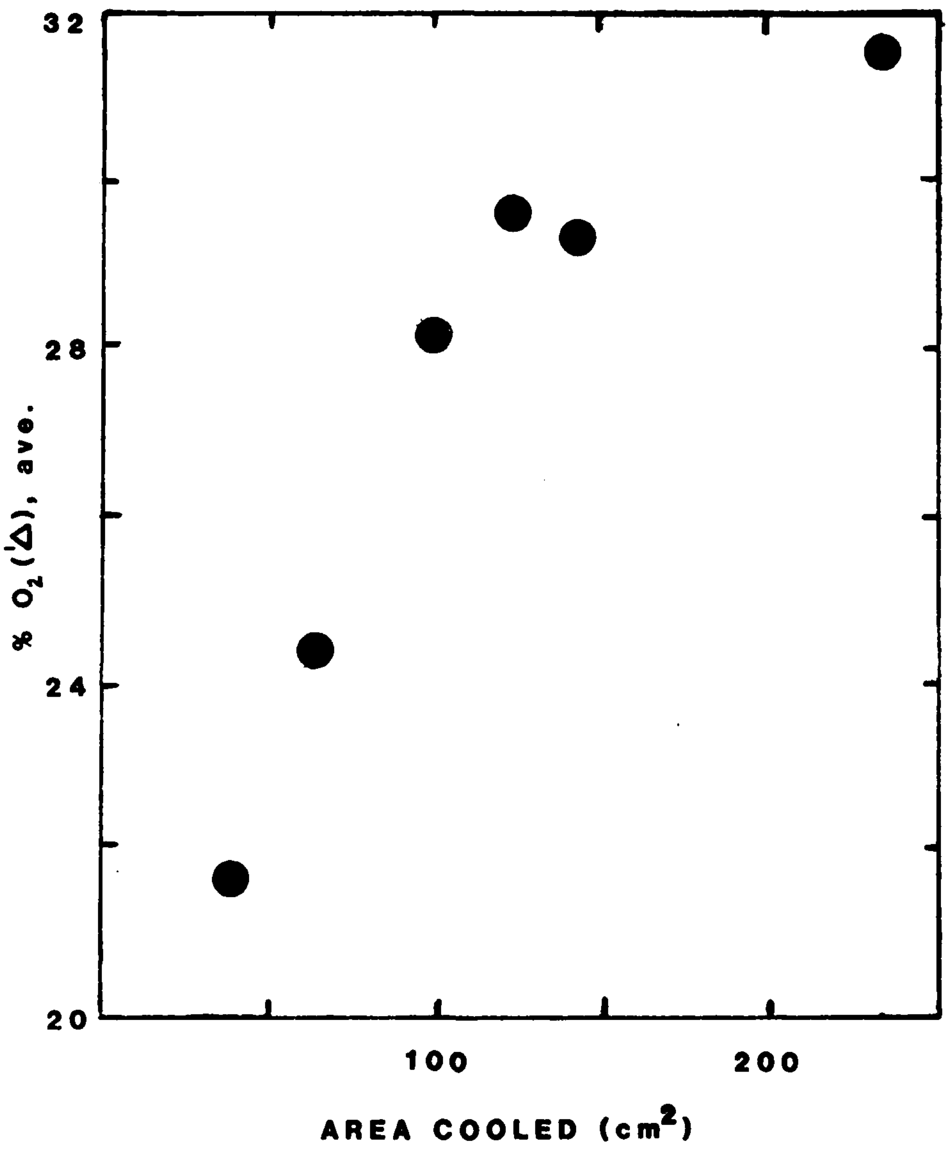

Fig 6. Plot of % $O_2(^1\Delta)$ average (for readings in first 10 minutes of each run) vs. area of in-reactor trap surface cooled to -78°C.

$O_2(^3\Sigma)$ is faster than the corresponding reaction with Cl^-, (Ref. 3, Vol. II, p. 46). The negligible effect of the Cl^- reaction on $O_2(^1\Delta)$ % in the generator output is supported by the results of the experiment in which added initial concentration of KCl to the basic H_2O_2 had no effect on $O_2(^1\Delta)$ production.

The effect of initial KOH concentration showed that this clearly was an important parameter in generator operation. How the KOH concentration affects the $O_2(^1\Delta)$ output is not obvious. If there were an optimum pH of the solution, then one might expect that as the pH of the more basic solution (12M KOH) was reduced by the generation reaction, the % $O_2(^1\Delta)$ would increase to the levels produced in the run in which the less basic (6M KOH) solution was used. Since this is not the case, other factors such as solution viscosity, rate of vaporization, competing reactions, and surface tension may also affect the $O_2(^1\Delta)$ production. Of course it is also clear that as the (12M KOH) run proceeded, H_2O_2 was consumed, and when the optimum pH was attained, the H_2O_2 concentration may have been sufficiently reduced to cause lower $O_2(^1\Delta)$ production rates.

Other aspects of the generator operation were observed to have fairly significant effects on $O_2(^1\Delta)$ production. In most runs, it was noted that if the Cl_2 flow was stopped for a short time and then resumed, the $O_2(^1\Delta)$ production for a few seconds after resumption of the flow was usually significantly higher than before the flow was stopped. This suggested that the trap surface may become more deactivating to $O_2(^1\Delta)$ or less effective in removing H_2O as the build-up of condensibles proceeds. Stopping the flow for a time may allow the surface on the trap to cool and harden so that more deactivators are trapped and higher $O_2(^1\Delta)$ %'s are observed when flow is resumed.

In certain runs where the trap coolant temperature was allowed to vary, it was found that the highest $O_2(^1\Delta)$ %'s were generally observed in the range -50 to -60°C. This range would probably differ for different reactor configurations, but its existence points again to the importance of trap parameters to effective generator operation.

Since two pumps were used, one with a 1.5 CFM capacity and the other at 15 CFM, a comparison of generator effectiveness as a function of flow rates could be obtained. Although the $O_2(^1\Delta)$ measurement technique (based on calibration using assumed % $O_2(^1\Delta)$ from a microwave discharge) cannot give absolute values, the measurements clearly indicated that the higher flow rates gave significantly higher $O_2(^1\Delta)$ % (from 12% to up to 40% with the higher flow rates). When this observation is combined with the observation that the depth of the Cl_2 injector in the solution had negligible effect on % $O_2(^1\Delta)$ produced, the major cause of $O_2(^1\Delta)$ loss must be attributed to deactivation during its transit from just above the reaction solution through the trap to the detector.

V. CONCLUSIONS

Our first major conclusion deals with the use of small-scale batch reactors to study the $O_2(^1\Delta)$ formation reaction. These low flow systems, with many interdependent operating parameters, are not likely to give quantitative information on the formation reaction or on the generator performance. Furthermore, the difficulty of controlling all parameters except for one under study limits interpretation of even qualitative observations. Thus our attempts to study the formation reaction shifted to theoretical calculations using the MNDO program[7].

Some general conclusions about reactor performance may be drawn. The major factor affecting $O_2(^1\Delta)$ yields coming out of the reaction solution appears to be the pH, or more directly, the relative concentrations of OH^- and H_2O_2. Once out of the solution, the $O_2(^1\Delta)$ undergoes losses whose magnitude is directly related to design of the in-reactor trap and the velocity with which it is transported to the detector.

Part 2. Excited I_2 Intermediate in $O_2(^1\Delta)$ - I_2 Dissociation Kinetics.

I. INTRODUCTION

A key issue in the chemical oxygen iodine laser (COIL) development is the kinetics of the dissociation of I_2 by $O_2(^1\Delta)$. Following analysis of laser operation of the COIL at the Air Force Weapons Lab [1, 2], it became obvious that the initially proposed mechanism for dissociation of I_2 by $O_2(^1\Delta)$ could not be the dominant one. That mechanism involved the so-called pooling reaction,

$$O_2(^1\Delta) + O_2(^1\Delta) \rightarrow O_2(^1\Sigma) + O_2(^3\Sigma),$$

followed by pumping of I_2 to a dissociative state, resulting in I atom formation:

$$O_2(^1\Sigma) + I_2 \rightarrow I_2^* + O_2(^3\Sigma)$$
$$I_2^* \rightarrow 2I.$$

The amount of undeactivated $O_2(^1\Sigma)$ in the laser flow was far too small to account for the I-atom formation observed. Subsequent work [8] showed that the rate of dissociation of I_2 by $O_2(^1\Sigma)$ is slower than it would have to be to account for observed dissociation rates.

An alternative mechanism involved the population of the $A'(2u\,^3\pi)$ state of I_2 by transfer from $O_2(^1\Delta)$ to ground state I_2, followed by additional transfer from $O_2(^1\Delta)$ to pump the $A'(2u\,^3\pi)$ state to a dissociative state of I_2. This mechanism seems unlikely in view of the observation[9] that the $A'(2u\,^3\pi)$state lies over 10000 cm^{-1} above the ground state while the $O_2(^1\Delta)$ state has approximately 8000 cm^{-1} of energy available. Recent results [10] indicate that the intermediate in the pumping of I_2 to a dissociative state may be vibrationally excited (up to $v=40$) ground state I_2.

Since the $A'(2u\,^3\pi)$ state of I_2 is expected to have an EPR spectrum in the range 17-24 kG, based on comparison with ground state I ($^2P_{3/2}$), we scanned this high field in an attempt to determine if the $A'(2u\,^3\pi)$ state plays any role at all in the dissociation process.

Our approach was to add Ar/I_2 mixtures to a flow of $O_2(^1\Delta)$ and obtain a profile of I* concentration as a function of distance from the mixing point. At a point before the peak in I* concentration, we scanned the high field for the EPR spectrum of $I_2 A'(2u\,^3\pi)$.

II. EXPERIMENTAL

1. Flow Apparatus. A diagram of the overall apparatus is shown in Fig. 7. As can be seen, $O_2(^1\Delta)$ and $O_2(^3\Sigma)$ were measured directly using their EPR spectra as previously described[11]. The chemical generator originally used in this flow system was similar in design and operation to the one shown in Fig. 3. Our experience in Part 1 led us to believe that the higher flow rates attainable in this system (with a 150 CFM pump) would result in yet higher $O_2(^1\Delta)$ %'s than the 30-40% we had observed using the 15 CFM pump. However, we could not achieve more than 20% $O_2(^1\Delta)$. Several modifications were made to the generator in an effort to improve $O_2(^1\Delta)$ % output. These included changes in the in-reactor trap position and capacity to minimize blockage by condensed materials and to ensure more even deposition of trapped materials, use of splash plates to keep cooling of the reaction solution by splashing contact with the trap to a minimum, and reducing the dead space in the reactor to minimize residence time of output gases in the reactor.

None of these alternations significantly improved the performance of the generator. Only when the trap configuration was changed to that shown in the generator diagramed in Fig 8, was it possible to obtain $O_2(^1\Delta)$ %'s in the 30-40% range with about 1 torr O_2 detected.

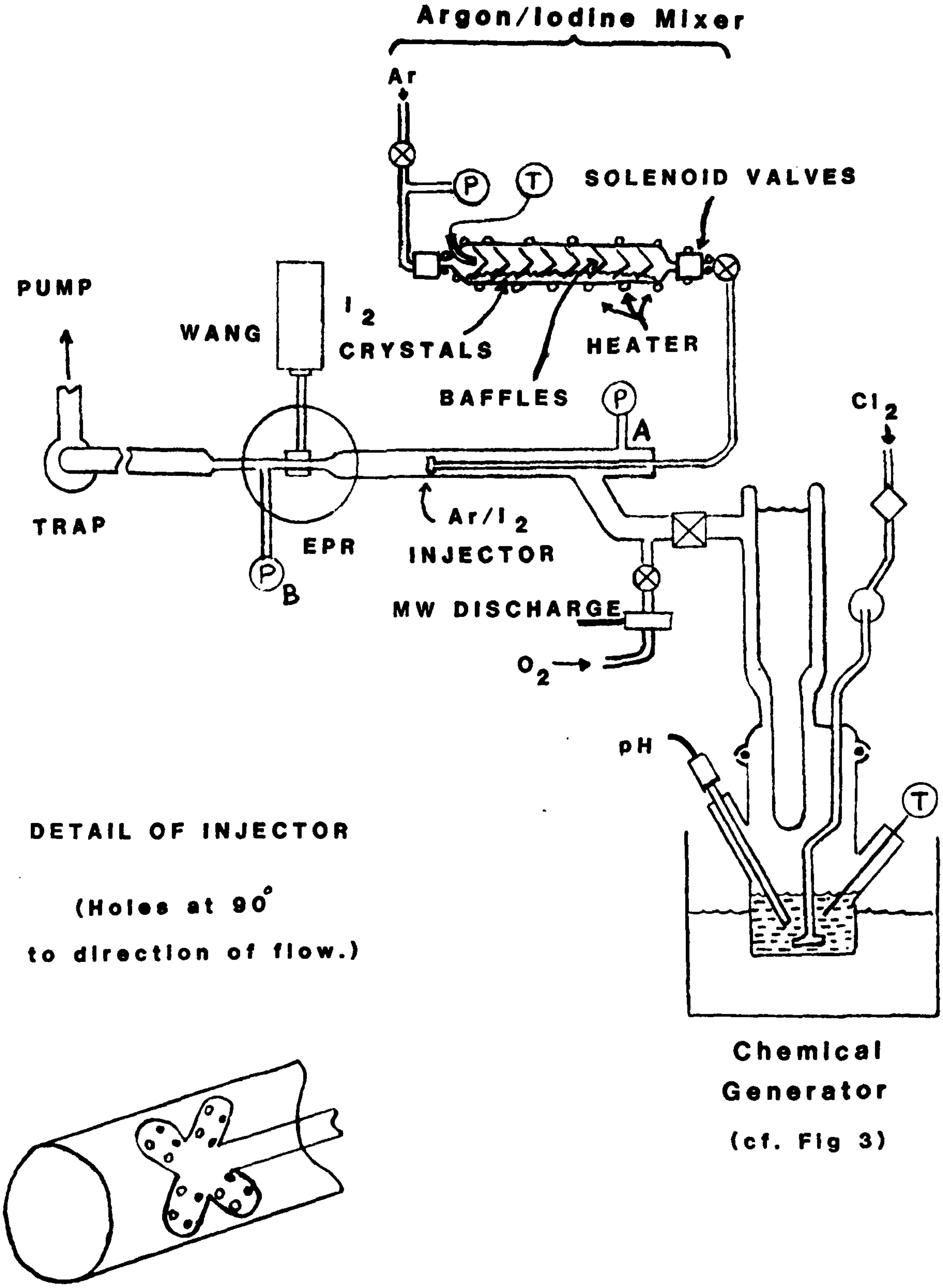

Fig 7. Flow system for EPR studies

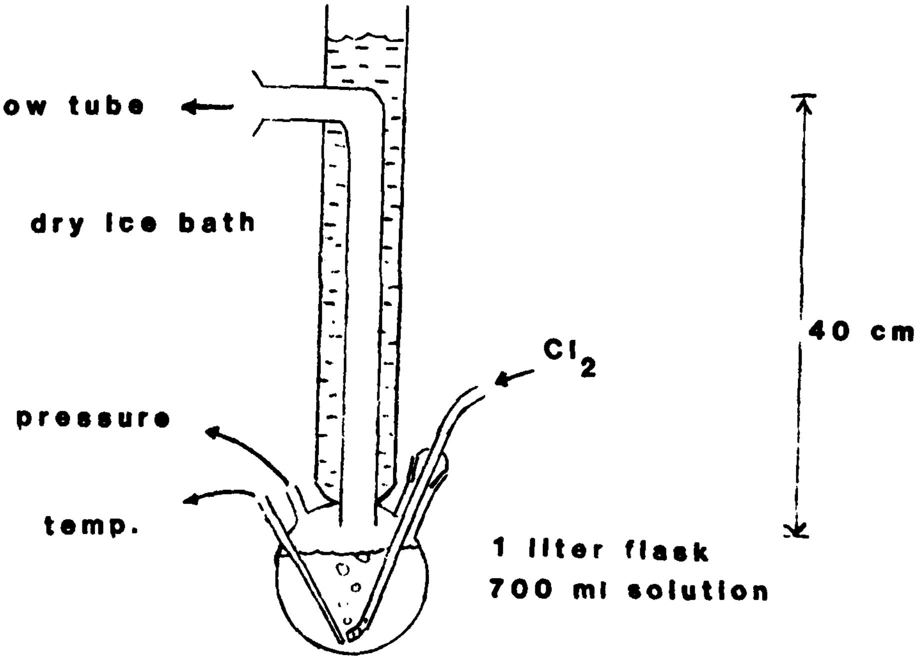

Fig 8. Batch reactor with flow-through trap configuration.

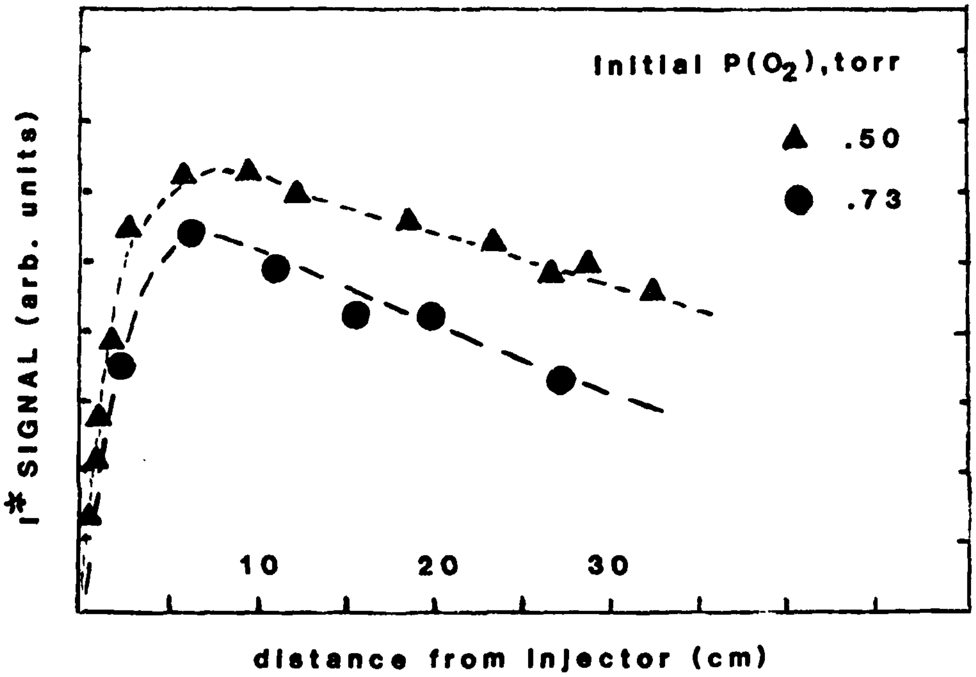

Fig 9. I* signal in EPR cavity as a function of distance from injector in flow tube. O_2 flow at 20 SCCS.

Molar flow rates for Ar and O_2 were measured (using a calibrated Matheson tube flowmeter) as a function of downstream pressures at points A and B (see Fig 7). The curves of downstream pressure vs molar flow rate of O_2 were used to determine molar flow rate out of the generator. It was also found that under the conditions used, the molar flow rate of O_2 was not detectably affected by adding Ar and vice versa. Thus once the molar flow rate out of the generator was measured, we could assume it was not changed by adding Ar (carrying I_2) into the flow in the quantities planned.

The movable injector was tested for its deactivating effect on $O_2(^1\Delta)$. It was found, using the microwave discharge to generate $O_2(^1\Delta)$ in O_2 flows, that the $O_2(^1\Delta)$ signal detected at the EPR cavity was not lowered by increasing the length of the nozzle in the flow tube until the nozzle was about 1 cm from the EPR cavity. Thus we were able to assume that the $O_2(^1\Delta)$ was not detectably affected by the nozzle position in the range, 1 cm - 30 cm from the EPR cavity.

2. Argon-Iodine Mixer (AIM). The AIM operated on the principle that the slow flow of Ar through the baffles in the AIM would ensure that the gas exiting the AIM would have partial pressures of I_2 : Ar in the ratio of the vapor pressure of I_2 at the temperature in the AIM : measured Ar pressure in the AIM. The baffles were funnels which fit tightly in the tube. The funnels were mounted on a glass center rod, and each had a 0.5 cm wide slit cut from its center to its edge. The slits were lined up at various angles to ensure thorough mixing. In runs in which we expected 0.2 - 0.3 torr of $O_2(^1\Delta)$ in the flow, we intended to keep the I_2 pressure added at less than 2% of $O_2(^1\Delta)$ pressure, or about 0.004 torr. Given 1.0 torr as a desired pressure of the Ar/I_2 in the flow, the required ratio of $Ar:I_2$ pressures in the AIM would be about 250:1. This was obtained by flowing Ar through the AIM at a pressure of 250 torr while maintaining the temperature in the AIM at 39°C (temperature at which $p(I_2) = 1$ torr). In practice, the temperature and pressure in the AIM were adjusted from these initial values to give the maximum I* signal at the cavity. The I* was detected using a liquid N_2 cooled Wang intrinsic germanium detector fitted with a

1.315 μm filter and connected to the EPR cavity by a light pipe. To determine the I* profile down the tube, $O_2(^1\Delta)$ was generated using a microwave discharge. Ar and I_2 from the AIM were injected into this flow of O_2. The I* signal was then recorded at various nozzle positions.

3. Scan of High-field EPR Spectrum. Using the generator shown in Fig 8 to produce $O_2(^1\Delta)$, scans of the EPR spectrum from 17 kG to 24 hG were made. Following system evacuation (down to 0.025 torr or less), the reactor was isolated and vented. Then 350 ml each of 6 M NaOH and 90% H_2O_2 were added. The reactor was then sealed and slowly pumped down. After the major part of the dissolved gases had escaped as indicated by decreased bubbling, the dry ice trap was filled and pumpdown continued at a faster rate. After stabilization of pressure and temperature (cavity pressure of about 0.05 torr and solution temperature between -20°C and -1[illegible]°C), Cl_2 was admitted to the reactor and measurements of pressure and EPR signals begun. After scans were made of the generator output with no I_2 added, the AIM was opened to admit Ar/I_2 into the flow, and the scans were repeated. The nozzle position was set at 5.0 cm from the EPR cavity based on I* profile data obtained using a microwave discharge to generate $O_2(^1\Delta)$ and adding Ar/I_2 under conditions similar to those in the chemical generator runs (Fig 9).

The Varian spectrometer used had an EPR V-3800 15-inch electromagnet (fitted with pole-caps to achieve the higher fields) and a 22.5 KW power supply.

III. RESULTS

The I* profiles shown in Fig 9 were obtained with microwave discharged O_2 at about 8-11% $O_2(^1\Delta)$. This I* vs distance profile is similar to those obtained at different and slower flow (and linear) velocities in other studies[12, 13, 14].

The high field (1.7 to 2.4 T) EPR spectra of the generator output with and without Ar/I_2 added to the flow gave no indication of the presence of any species besides O_2. During generator operation, the parameters shown in Table II were measured.

Table II. Generator Operation for High Field Scans

No Ar/I_2 added:

P (cavity): 0.90 ± 0.02 torr

P (flow tube): 1.70 ± 0.04 torr

% $O_2(^1\Delta)$: 25 ± 2%

linear velocity in flow tube: $(3.8 \pm 0.3)\mathrm{x}10^3 \mathrm{cms}^{-1}$

Ar/I_2 added:

P (cavity): 0.96 ± 0.02 torr

P (flow tube): 1.78 ± 0.04 torr

P (AIM): 80 torr

T (AIM): 33°C

On the basis of these data and other observations on this flow system, we estimate that with the Ar/I_2 flowing, $P(I_2)=0.003$ torr and $P(O_2(^1\Delta))=0.15$ torr at the mixing point. The spectra of the generator output were also compared to the spectra of O_2 flowing through a microwave discharge. $O_2(^1\Delta)$ lines in the spectra could be identified by noting which lines disappeared when the microwave discharge was turned off. Four of the lines identified for the J=3 level of $O_2(^1\Delta)$ were previously reported by Miller [15]. We also observed two others at higher fields which he could not observe, and these are shown in Table III along with the previously reported lines. We report the $(h\upsilon/\mu_B H)=g_{exp}$ values obtained from Miller's data since his H and υ values were precisely determined. The g_{exp} values reported for the additional two lines we observed were obtained by extrapolating a least-squares fit (correlation coefficient of 0.99994) of Miller's g_{exp} values with our H values. Our calculated g_{exp} values using υ=9.149 G Hz differ by about 1% from Miller's with the principal error expected to be in our H values.

Table III. J=3 Level EPR Spectrum of $O_2(^1\Delta)$

M (M → M + 1)	H, T	$h\nu/\mu_B H$	
-3	1.9054	0.34593	
-2	1.9264	0.34221	
-1	1.9529	0.33760	
0	1.9872	0.33181	
1	2.0333	0.32380	extrapolated values
2	2.0977	0.31269	

IV. DISCUSSION

Based on the comments in the INTRODUCTION, it is not surprising that an EPR spectrum of the $A'(2u\,^3\pi)$ state of I_2 was not observed. However, it should be noted that our results indicate only that the presence of this state is not detectable in our flow system. The concentration of I_2 in the region of the flow we were observing could not have been greater than 0.001 torr. At best only a fraction of this would be expected to be in the $A'(2u\,^3\pi)$ state (if it is formed at all). These and other limitations of using a batch type chemical generator to study the $O_2(^1\Delta)/I_2$ dissociation kinetics are significant indeed, with trap effectiveness and in-reactor residence times being the crucial sources of the limitations. A clearer illustration of the problems associated with reactor performance was our observation that the % $O_2(^1\Delta)$ did not increase when our small scale generator (used in Part 1) was used on the higher flow rate system (going from a 15 CFM to 150 CFM pump).

In fact there was a decrease in % $O_2(^1\Delta)$ which may be due to the fact that at the higher flow rates, a significantly higher pressure must be maintained in the reactor to produce the same O_2 pressure downstream in the detection system. Thus the shorter transit time from reactor to detector may have been more than offset by the higher pressure in the more hostile environment in the reactor and trap. A small-scale generator chemically engineered to produce stable, impurity-free flows at higher O_2 pressures and $O_2(^1\Delta)$ %'s is needed to pursue this effort. Some progress has been made in this direction.[16].

V. CONCLUSIONS

Our investigation yielded no evidence that the $A'(2u^3\pi)$ state of I_2 can be detected by EPR in the output of a small scale $O_2(^1\Delta)$ generator to which Ar/I_2 has been added. The previously unreported $M \longleftrightarrow M + 1$ transitions $1 \longleftrightarrow 2$ and $2 \longleftrightarrow 3$, of the J=3 level of $O_2(^1\Delta)$ have been detected and g_{exp} values calculated.

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