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CONTINUATION OF LABORATORY CHEMILUMINESCENT EXPERIMENTS FOR BALLISTIC MISSILE DEFENSE

NEVILLE JONATHAN
PETER WARNECK

FINAL REPORT

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PREPARED FOR
AIR FORCE CAMBRIDGE RESEARCH LABORATORIES
OFFICE OF AEROSPACE RESEARCH
UNITED STATES AIR FORCE
BEDFORD, MASSACHUSETTS

SEPTEMBER 1964

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GEOPHYSICS CORPORATION OF AMERICA
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ABSTRACT

The chemiluminescent emission arising from the reactions of atomic oxygen with acetylene, ethylene, methane and carbon monoxide has been investigated in the pressure range 1 - 1000 microns Hg. In a separate study, the reactions of oxygen atoms with acetylene, ethylene and carbonyl sulfide, have been investigated mass spectrometrically. The reaction of atomic oxygen with acetylene has been emphasized in both studies. The present report contains among various results, data on the pathway of the initiation reaction; the associated rate constant; the variation of atomic oxygen concentration, acetylene concentration and carbon monoxide concentration with time; the intensity dependence of the various chemiluminescent emissions on time and on molecular oxygen concentration.

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GENERAL INTRODUCTION

This Final Report describes the experimental work performed under Contract AF19(628)-3320 covering the period August 21, 1963 to August 20, 1964. The major objective of these studies has been to simulate the conditions which exist in the atomic oxygen region of the upper atmosphere when missile trail gases are released.

The characteristic chemiluminescent missile trails show strong CH emission bands which are evidently the result of reaction of atomic oxygen with hydrocarbon fuel products. It is known that the most reactive hydrocarbons with atomic oxygen are those which are unsaturated. It is evident that considerable quantities of these gases are liable to be present in the trail of a missile which as a hydrocarbon fuel, both as a result of partial cracking and oxidation of the parent fuel and as a result of incomplete use of the fuels themselves. In an attempt to understand the mechanisms by which this chemiluminescence occurs, we have attempted to simulate the conditions which exist and to carry out experiments with the simplest model hydrocarbons under controlled conditions. We have chosen acetylene (C_2H_2), ethylene (C_2H_4), and methane (CH_4) as being representative of the triple, double and single bond hydrocarbons, respectively.

The experimental program has been divided into two parts. One part has involved the study of the reaction rates using a fast flow system with a continuous sampling mass spectrometer. The other has involved light emission studies using spectroscopic techniques.

The following people have actively contributed to the research described here:

Neville Jonathan
Joseph Padur
John Sullivan
Peter Warneck

They wish to acknowledge the skilled technical assistance and helpful comments of many of their colleagues.

SECTION 1

SPECTROSCOPIC STUDIES OF LIGHT EMITTING REACTIONS CARRIED OUT UNDER CONDITIONS DESIGNED TO SIMULATE THOSE EXISTING IN THE UPPER ATMOSPHERE DURING THE EARLY STAGES OF MISSILE LAUNCHES

Light emission from missile trails is characteristic of the early stages of missile launches, particularly in the cases of those rockets which rely on hydrocarbon fuels. There is good reason to believe that a large proportion of the light emission is chemiluminescence. This must arise mainly from the reaction of atomic oxygen and ozone with the unspent hydrocarbons or some of their oxidation by-products. It is also possible that some emission may occur as a result of the chemiluminescent reactions of atomic nitrogen with the exhaust gases.

In the Final Report of the previous contract, AF19(628)-231, we gave details of survey experiments which we had carried out. From these data it seemed apparent that most light emission was associated with the most highly unsaturated hydrocarbon reactions and that light emission decreased as the ratio of carbon to hydrogen in the molecules decreased. This was true for the reactions with both atomic oxygen and atomic nitrogen. On the basis of this study we have chosen the model compounds acetylene (C_2H_2), ethylene (C_2H_4) and methane (CH_4) as representative of the triple, double and single bond hydrocarbons, respectively. Since the most highly unsaturated hydrocarbon must be responsible for most of the light emission, the most extensive studies have been made on acetylene with a somewhat lesser emphasis placed on ethylene. In addition, studies were made of the chemiluminescent reactions of oxygen atoms with carbonyl sulfide, nitric oxide, and carbon monoxide.

1.1 APPARATUS AND EXPERIMENTAL METHODS

1.1.1 Medium Pressure Flow Tube Apparatus. The apparatus used in the 500 micron region was of the fast flow reaction tube type and is shown in block diagrammatic form in Figure 1. Using this system it was possible (with minor modifications in some cases) to make: (1) atomic oxygen in the presence of molecular oxygen by discharging oxygen, (2) atomic oxygen in the presence of very little molecular oxygen by discharging a 99:1 mixture of argon and oxygen, (3) atomic oxygen in the absence of the molecular form by discharging nitrogen and titrating the atoms thus formed with nitric oxide whereupon the very fast reaction ($\sim 10^{-11}$ cc molecule^{-1} sec^{-1}) occurred

$$N + NO \rightarrow N_2 + O$$

The flow tube dimensions were such that the linear velocities of the gases were of the order of 1,000 cm/sec. while it is known that

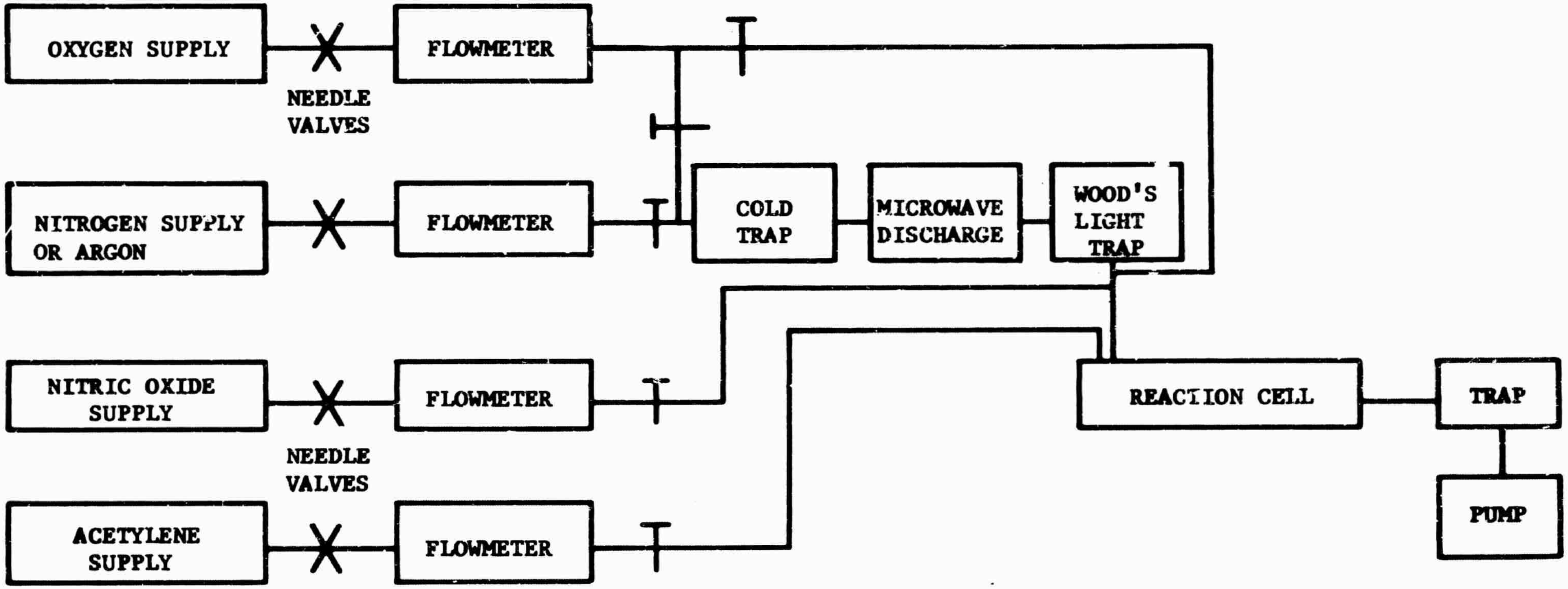

Figure 1. Block diagram of apparatus for observing chemiluminescence.

the time for an allowed electronic transition is between 10^{-6} and 10^{-8} sec. In particular the lifetimes of the $A^2\Delta$ and $B^2\Sigma^-$ states of CH are of the order of 10^{-6} sec.(1) and that of the $A^3\pi_g$ state of C_2 is about 10^{-7} sec.(2) The sources of some of the other emissions are unknown but it is highly probable that the lifetimes will be much shorter than the time taken for the gas to travel 1 cm. Hence, it can be seen that the light emission due to any particular source will occur virtually at that point where the source was formed. This radiation is therefore essentially a measure of the rate of formation of the emitting species at that point and after that reaction time.

1.1.2 Low Pressure Apparatus. A detailed description of this apparatus is given in the Final Report of Contract AF19(628)-231, GCA Technical Report 62-25-A. Hence, only a brief description will be given here. The system by which the atomic species were produced was similar to that shown in Figure 1. The reaction cell was a 50-liter, 3-necked Pyrex flash shown diagrammatically in Figure 2. It was continually evacuated by a large Welch mechanical pump (15 cu ft/min) and a NRC 4 inch oil booster pump which had a maximum pumping efficiency between 1 and 100 microns Hg. A liquid nitrogen trap was maintained between the cell and the booster pump at all times. The cell pressure was measured by a McLeod gauge. The pressure was measured at various points in the cell and found to be identical indicating that no pressure gradient was set up by the gas flow. This

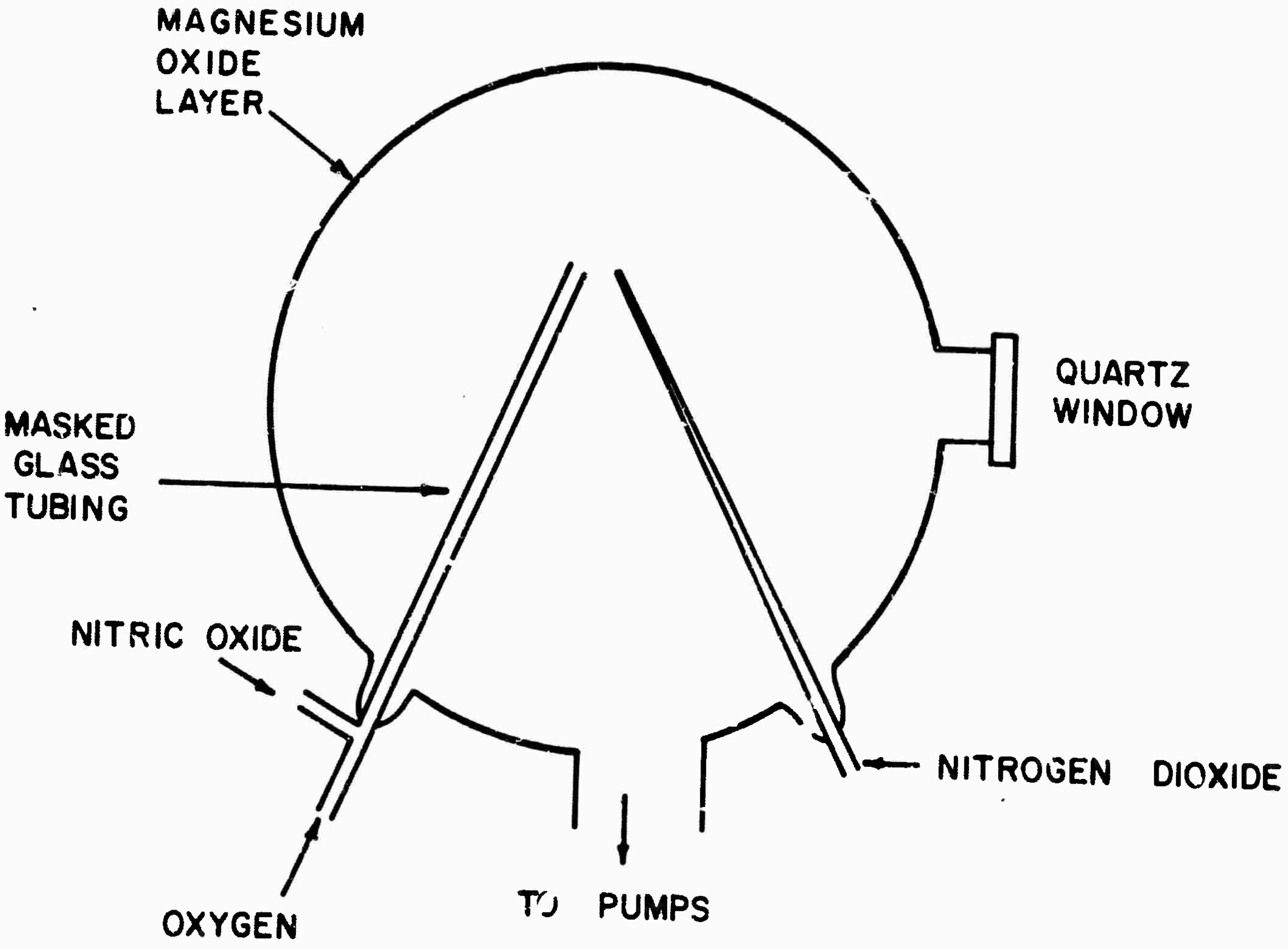

Figure 2. Diagram of low pressure reaction cell.

was also checked by pointing the McLeod tube opening towards the gas flow and directly away from it. Again identical readings were obtained. Yet another indication of the lack of appreciable pressure gradient was given by the appearance of a uniform luminescence in the cell when a premixed flow of atomic oxygen and nitric oxide was added. In normal use the cell was coated by a layer of magnesium oxide in order to increase the light gathering efficiency.

1.1.3 Detection Equipment. The spectrum of the light emission was obtained where possible using a Perkin-Elmer single beam double pass spectrometer. Background noise was kept to a minimum by chopping the incoming light beam on its second pass at a fixed frequency of 13 cps. The a.c. signal resulting at the detector was then fed into an amplifier tuned to this frequency. The spectrum region under observation was scanned automatically at a predetermined speed. The spectra were recorded using a Leeds and Northrup 10 millivolt recorder. The detector used was an E.M.I. 9558B photomultiplier tube fitted with a quartz window and was designed for use in the region 2500 to 7500 Å. A special preamplifier was used to minimize electrical pick-up.

On occasion, particularly with the low pressure apparatus, it was desirable to measure the intensity of the over-all light emission. These measurements were made with either a RCA 1P28 photomultiplier (S5 cathode) or EMI 9558B photomultiplier (S20 cathode) coupled to a Victoreen microammeter. Checks were made to ensure that the microammeter and photomultiplier gave linear readings over the scales in which they were employed.

1.2 RESULTS

1.2.1 The Reaction of Atomic Oxygen with Acetylene. It is well known that the main emission occurring as a result of the reaction arises from C_2, CH, and OH radicals and a considerably lesser contribution from the CHO radical. In addition, there is significant continuous emission from an unidentified source with a short wavelength cut off at approximately 3965 Å. Further emission occurs outside the wavelength range covered in the present studies, namely in the infrared and in the vacuum ultraviolet spectral region.

While the studies described in the last Final Report were carried out in the presence of large quantities of molecular oxygen, it was one of the aims of the present study to investigate the reaction in the absence of molecular oxygen and to determine the effect of O_2 on the light emission. As was mentioned earlier, this was accomplished by discharging a 99:1 ratio of argon and oxygen or by making the oxygen atoms by titrating atomic nitrogen with nitric oxide. Most of the results were described in detail in the semi-annual report under this contract dated 20 January 1964, and 20 July 1964. Hence, it suffices to give a brief summary here.

The rate of formation of the excited species in the absence of molecular oxygen was investigated using the medium pressure flow apparatus. Spectra were obtained of the light emission at regular time intervals up to 15 milliseconds after mixing. The area under a band system as measured by a planimeter was taken as being proportional to the light emission from the particular radical at that time. A typical plot of the results is shown in Figure 3a. It was found in all cases investigated that the maximum amount of excited CH is formed at earlier times than the maximum amount of the unknown emitter of the continuum. The C_2 swan bands are formed by a slower reaction than either of these. The fall off of the CH system at 4300 Å and 3900 Å is identical within experimental error and the same also holds true for the C_2 bands at 4700 Å and 5100 Å. It is thus suggested from the above that the CH systems at 3900 Å and 4300 Å were formed from the same reactions at the same rate. Similarly, it is suggested that the C_2 bands are formed predominantly by one reaction.

The addition of molecular oxygen upstream of the mixing region had two effects: (a) the C_2 bands, the CH bands and the continuum were strongly quenched and (b) the OH system at 3064 Å became evident. A typical plot of the data is shown in Figure 3b which is the sister graph of Figure 3a. It is seen that the maximum excited OH is formed at a time between that of C_2 and the emitter of the

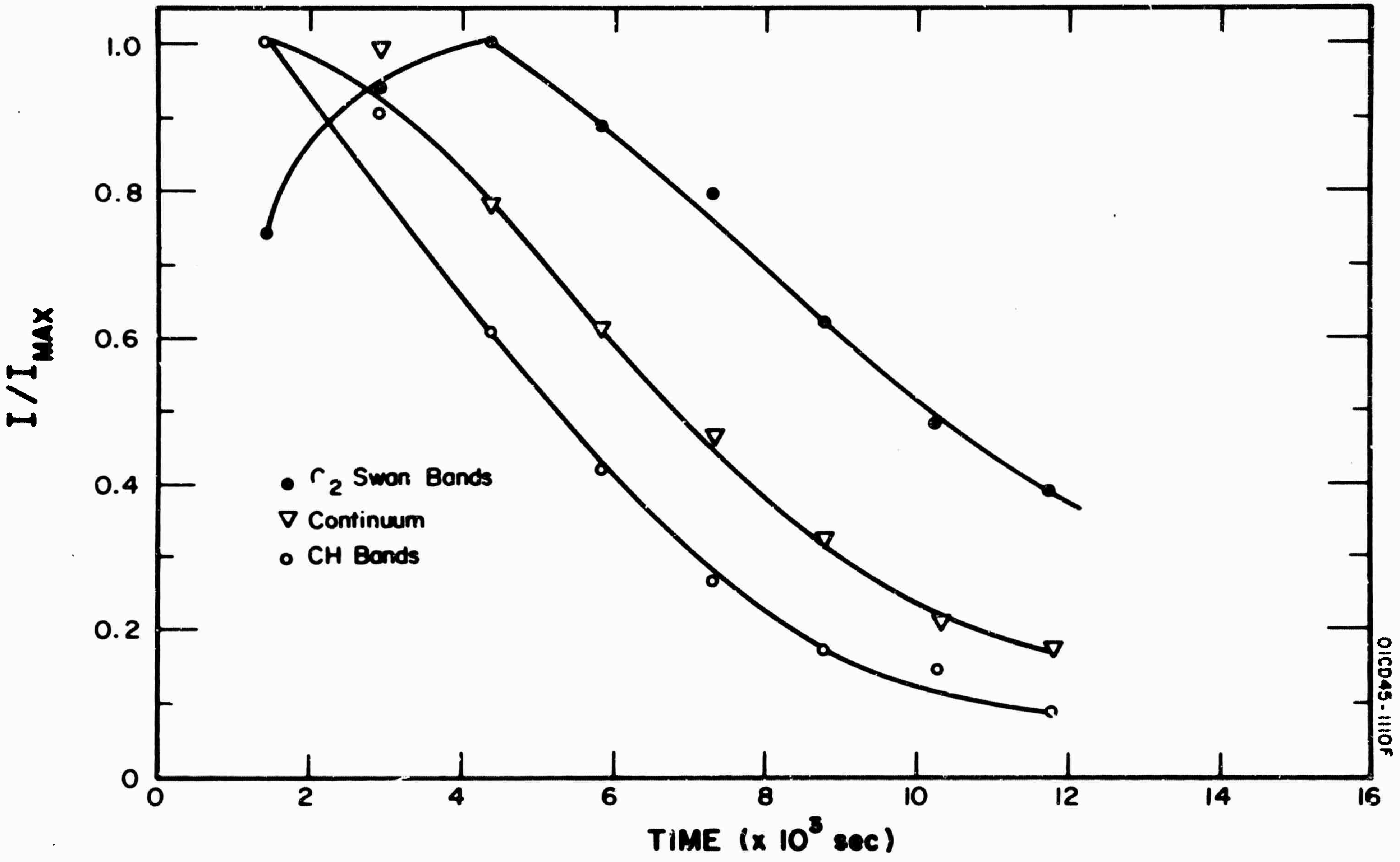

Figure 3a. Reaction of acetylene with atomic oxygen (made from N + NO) formation of emitters in the absence of molecular oxygen.

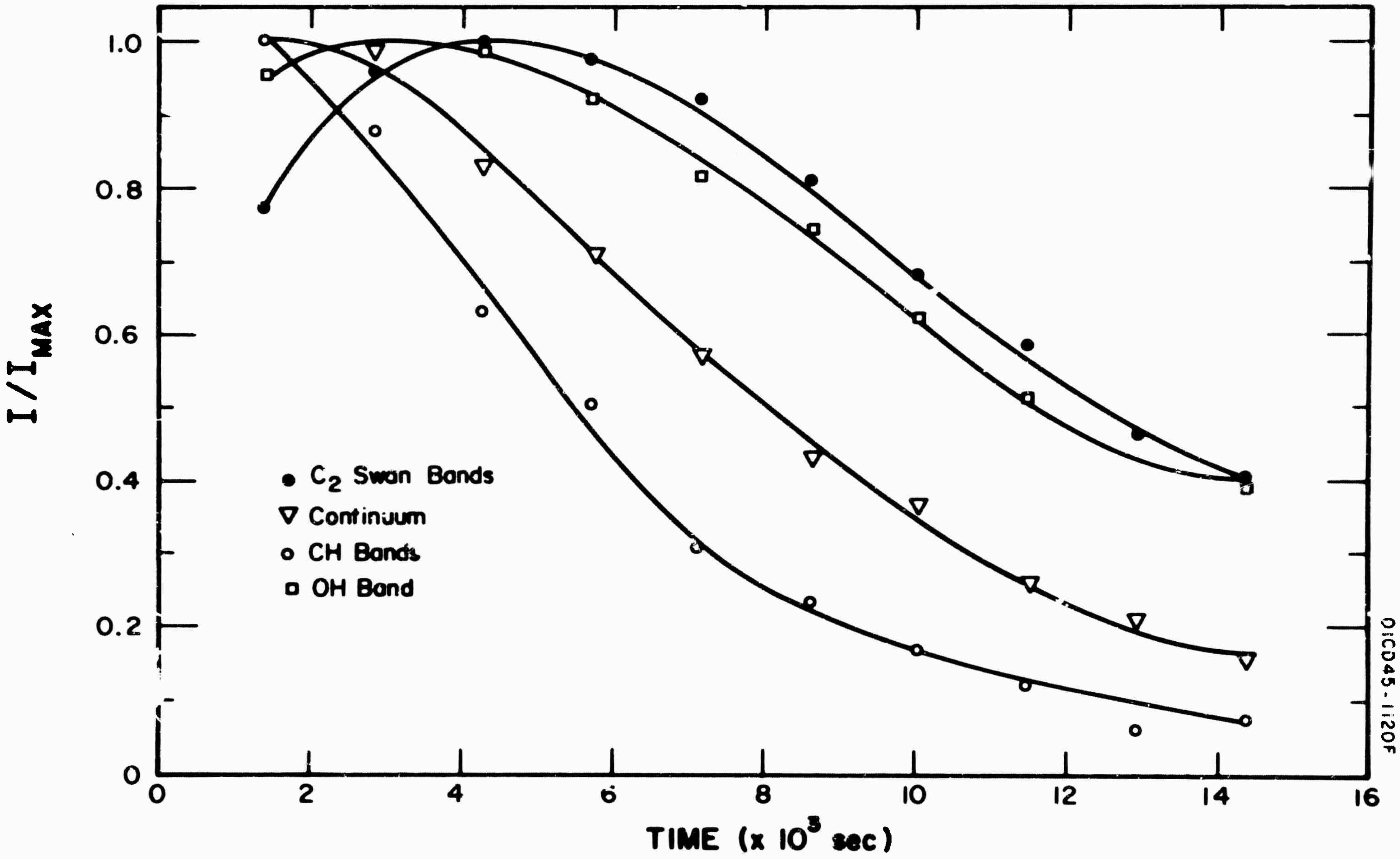

Figure 3b. Reaction of acetylene with atomic oxygen (made from N + NO) formation of emitters in the presence of 2% molecular oxygen.

continuum. Similar results were obtained also when atomic oxygen was produced by discharging a 99:1 mixture of argon and oxygen (for detail see semi-annual report dated 20 July 1964).

A few experiments were also made using molecular oxygen as the predominant third body. It was found that the order of formation of the species was similar to that found using the other two methods, indicating that the mechanism of chemiluminescence is not basically different in the presence of large amounts of O_2 when compared to its absence.

1.2.2 Quenching of Emission by Molecular Oxygen, Nitric Oxide and Carbon Dioxide. A series of experiments were carried out to investigate the quenching efficiencies of molecular oxygen and nitric oxide (which are free radical scavengers) and carbon dioxide (which is not). Additions of each gas were made in turn in amounts up to approximately 2% of the total flow and the intensity of the various bands was measured. It was found that carbon dioxide gave only a slight quenching effect which was of the order of 5%, but oxygen and nitric oxide were both very efficient quenchers. The relative efficiency of nitric oxide as a quencher is shown in Figure 4. It should be noted that in addition to its effect as a quencher, nitric oxide gives rise to CN and NH bands at 3590 Å and 3360 Å. No detailed investigation of the relationship has been performed but the implications were discussed in a previous report. The relative efficiency

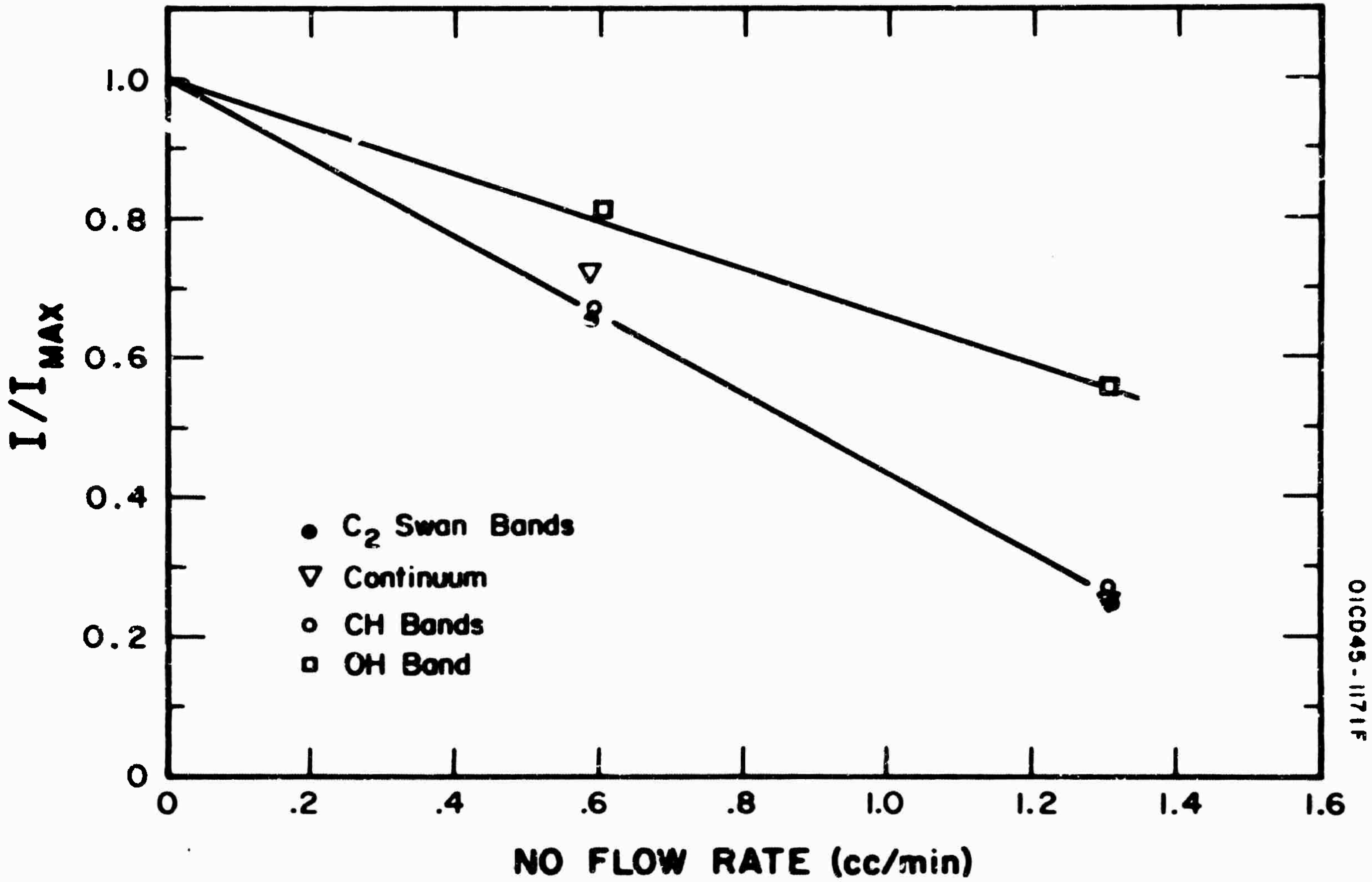

Figure 4. Effect of nitric oxide addition on emission.

of molecular oxygen as a quencher is shown in Figures 5a and 5b for reaction times of approximately 3 and 8 milliseconds, respectively. Comparison shows that the quenching is less at the later timer. Also shown in the figures is the rate of OH emission produced. A linear relationship with oxygen concentration is evident. Since in these experiments oxygen atoms were produced by discharging an oxygen - argon mixture, some molecular oxygen was already present even when no additional O_2 was admixed. This accounts for the observation that the OH emission does not drop to zero as the flow of O_2 admixture is shut off. These results are consistent with the following interpretation: (a) the OH emission is due to the reaction $CH + O_2 \rightarrow CO + OH^*$, the CH radical being in the ground state, (b) quenching of the other emitters upon admixture of O_2 or NO is produced by radical scavenging, involving an as yet unidentified intermediate species. This has been discussed in detail previously.

1.2.3 Effect of Chemi-ionization upon the Emission. The possible effect of ions known to be produced in the oxygen atom — acetylene reaction as a consequence of chemi-ionization has been briefly investigated. For this purpose, a flow tube was constructed containing two parallel electrode plates in the vicinity of the reaction space, the spacing being 1 cm. The voltage across these plates was varied from 0 - 200 volts while the reaction was in progress. No changes in the light emission could be noted

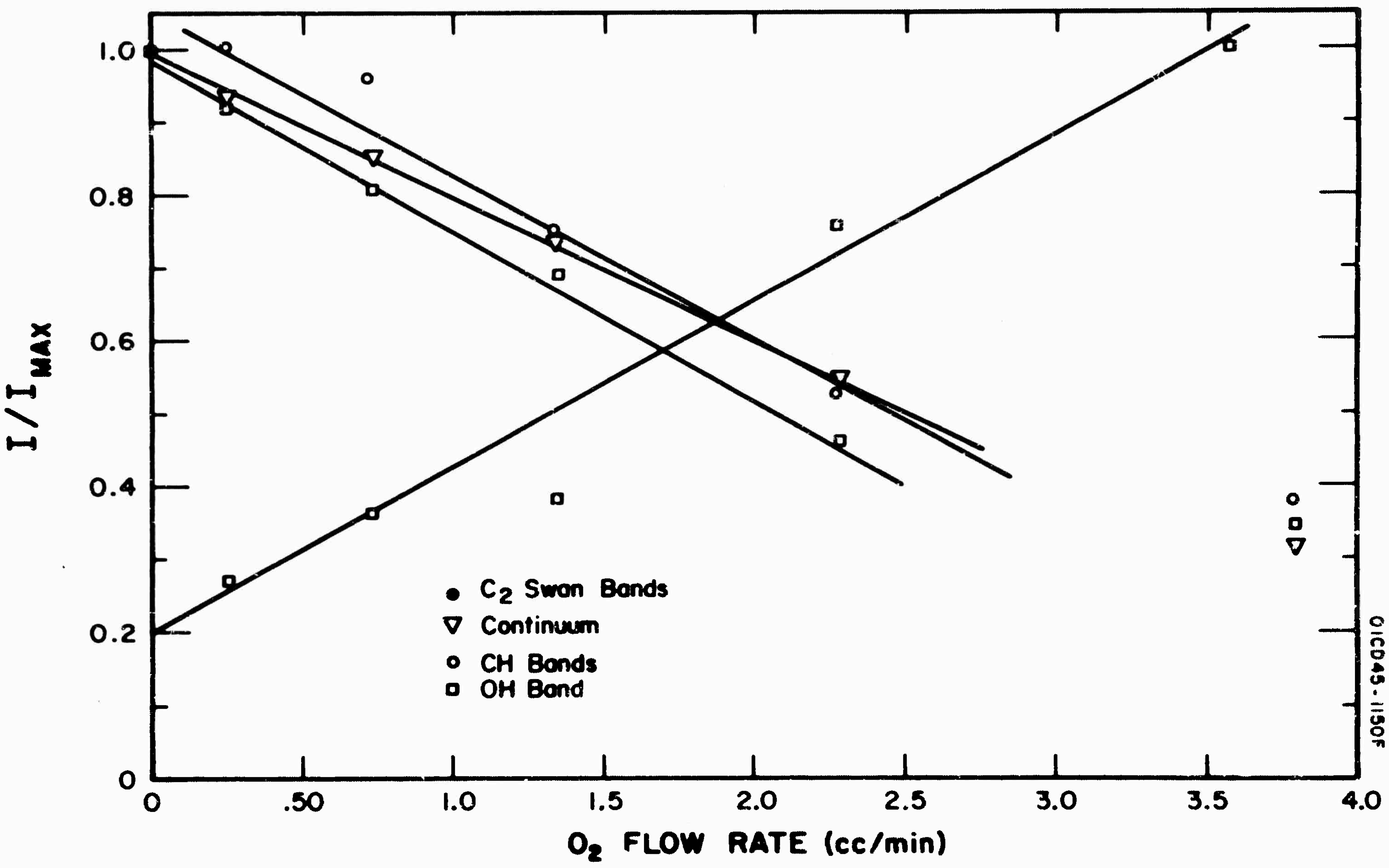

Figure 5a. Effect of molecular oxygen on emission after 1 millisecond.

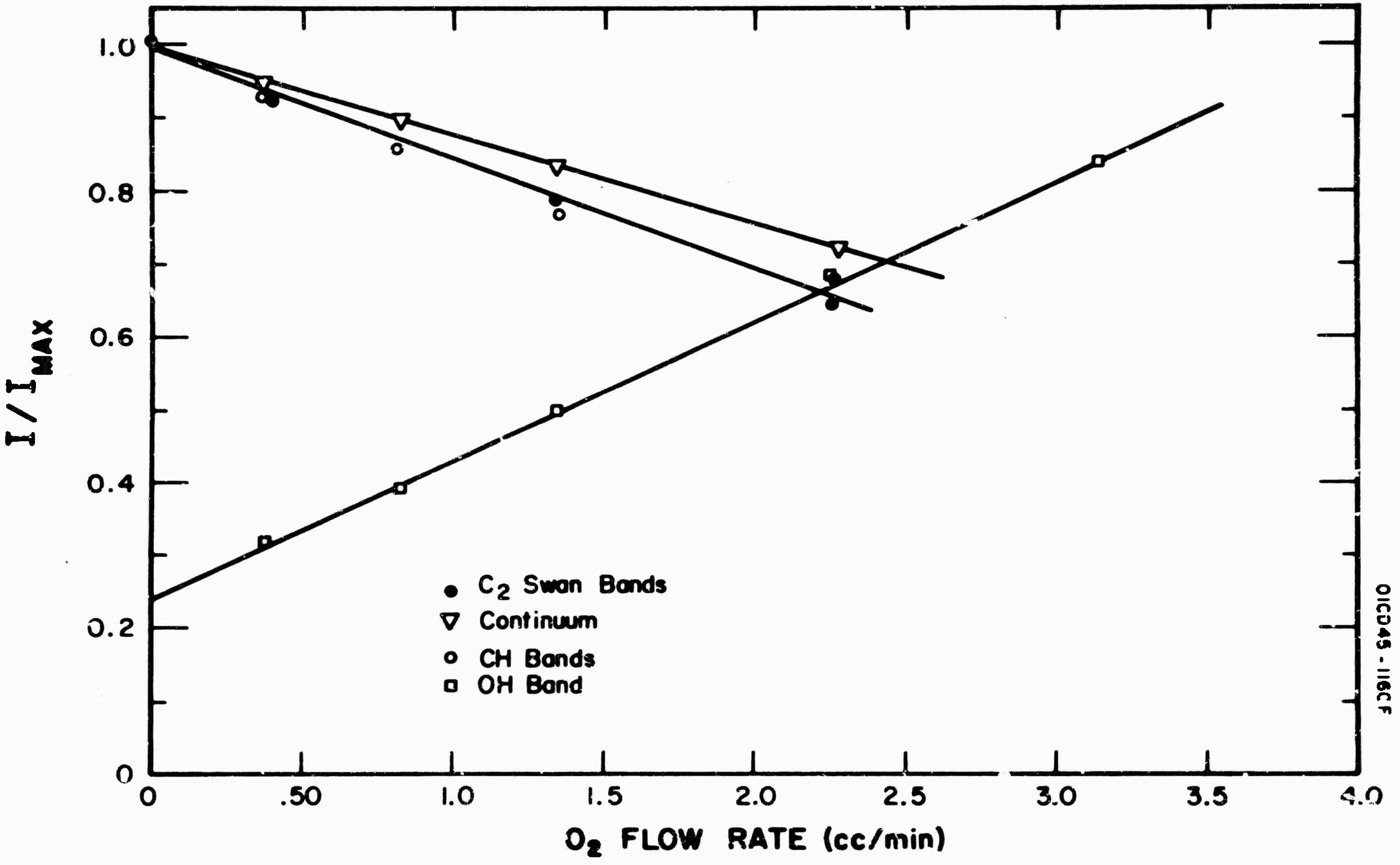

Figure 5b. Effect of molecular oxygen on emission ~ 8 milliseconds later.

concerning the C_2, CH, OH bands or the continuum. When the voltage was increased to more than 200 volts a breakdown occurred resulting in a gas discharge. This experiment demonstrates that the principal emissions are not the result of ion reactions, and also that ions are not involved in producing the continuum.

1.2.4 Effect of Discharged Argon upon Acetylene. It has recently been noted that if argon was passed through a microwave discharge and then mixed with acetylene a luminescence resulted.(3) It is believed that some high energy states of argon which possess a long lifetime are responsible for the decomposition. In a brief study of this phenomenon, it was found that the main emission occurred from the CH and C_2 systems and the continuum which was in agreement with the previous investigation.(3) The intensity of this emission is at least a factor of 10^3 less than that observed with atomic oxygen and argon and so does not interfere in any way with those measurements. It is interesting to note from Figure 6 that the order in which the emissions appear as a function of time is the same as in the O-atom acetylene reaction. This would seem to indicate that essentially the same mechanisms are responsible for the emission in both cases. Significantly, the OH band at 3064 Å could also be produced by the addition of molecular oxygen. There were some marked changes in intensity of the bands, however. Nevertheless, these observations indicate that the emitter of the continuum

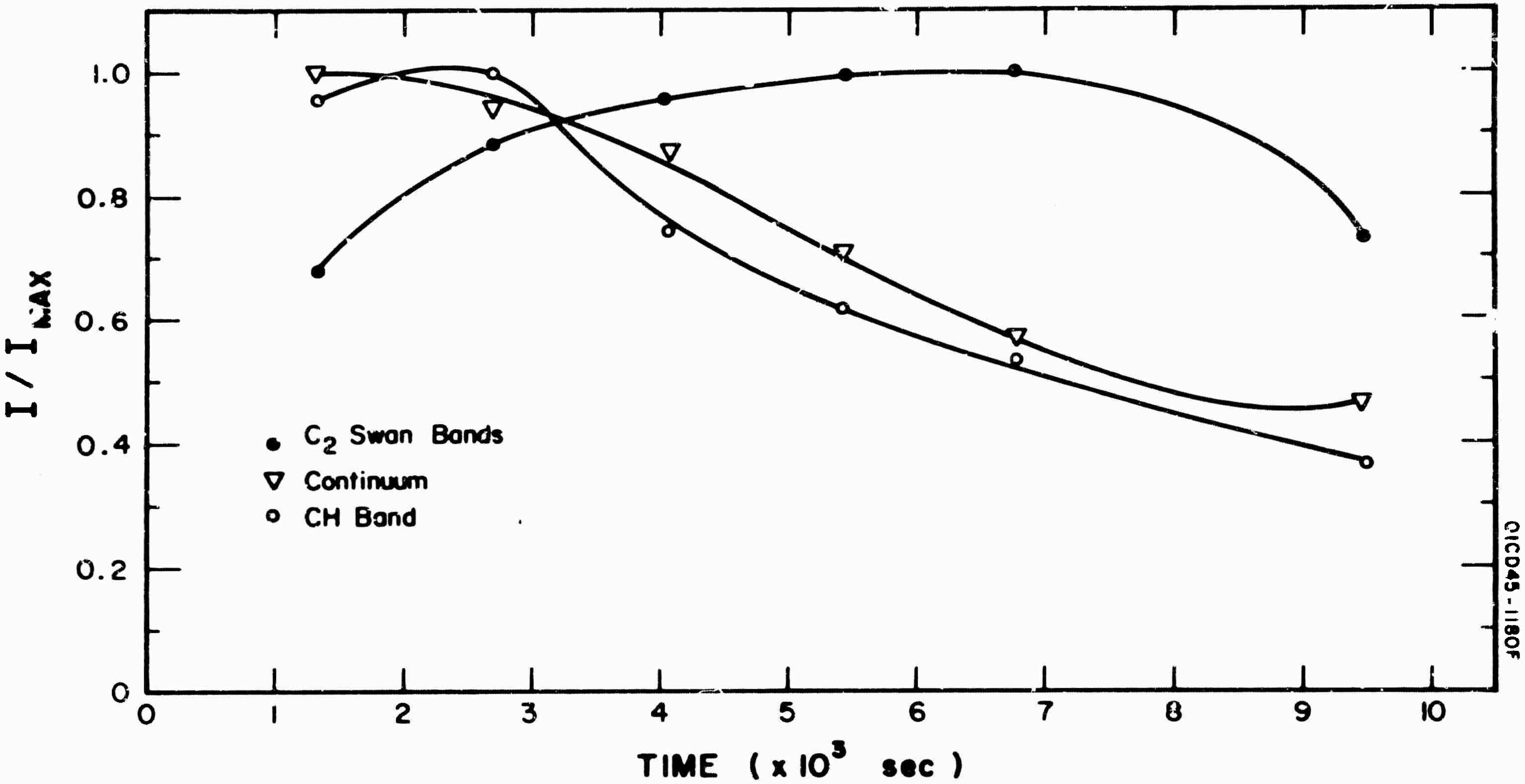

Figure 6. Emission from the decomposition of acetylene by argon as a function of time.

does not contain oxygen and, hence, the likely emitter is a fragment of the acetylene molecule itself.

1.2.5 Spectral Distribution of the O + C_2H_2 Chemiluminescence. In these experiments the spectra obtained were corrected for the spectral response of the instrument. The spectrometer was first calibrated over the spectral region 3600 Å to 7000 Å using a stable source of known flux and spectral distribution. This source which was a tungsten ribbon filament lamp had itself been calibrated by a N.B.S. standard light source. A check on our calibration was made by recording the spectrum of the atomic oxygen — nitric oxide light emission over this wavelength region. The spectral intensity at various wavelengths was corrected by multiplying by the ratio of the N.B.S. response of the tungsten lamp to that of the spectrometer response at the same wavelength. The resulting curve for the spectral distribution of the O + NO chemiluminescence was compared with the known data (4) and was found to be in good agreement.

The true spectral distribution of the O + C_2H_2 chemiluminescence over this wavelength range was measured in the same manner. The results were presented in the semi-annual report dated 20 July 1964. The considerable variation of the intensity distribution with reaction time does not warrant republication at this place.

1.2.6 Infrared Radiation. A qualitative investigation was undertaken to examine the possibility that the reaction of acetylene with atomic oxygen produced significant vibrational excitation and hence infrared radiation. A lead sulfide detector was used and any signals were detected on an oscilloscope. It was found that the reaction gave significant radiation even beyond 2 microns. No attempt was made to identify the emitter or emitters but this is obviously in the fundamental frequency range and one can tentatively suggest carbon monoxide as a likely source.

1.2.7 The Reaction of Atomic Oxygen with Ethylene. The light emission produced by the reaction of atomic oxygen with ethylene is well known to be considerably less than that from the corresponding acetylene reaction. However by suitable adjustment of spectrometer settings, it has proved possible to make some spectroscopic observations of the emission.

It was found that, under all conditions, the only detectable radiation between 3000 and 6300 Å arose from the OH band systems, the 4300 Å CH band and a very weak emitter of what is probably a continuum in the visible. The spectral distribution of the radiation is shown in Figure 7.

The addition of molecular oxygen considerably quenched the CH emission at 4300 Å but had a much smaller effect on the OH emission

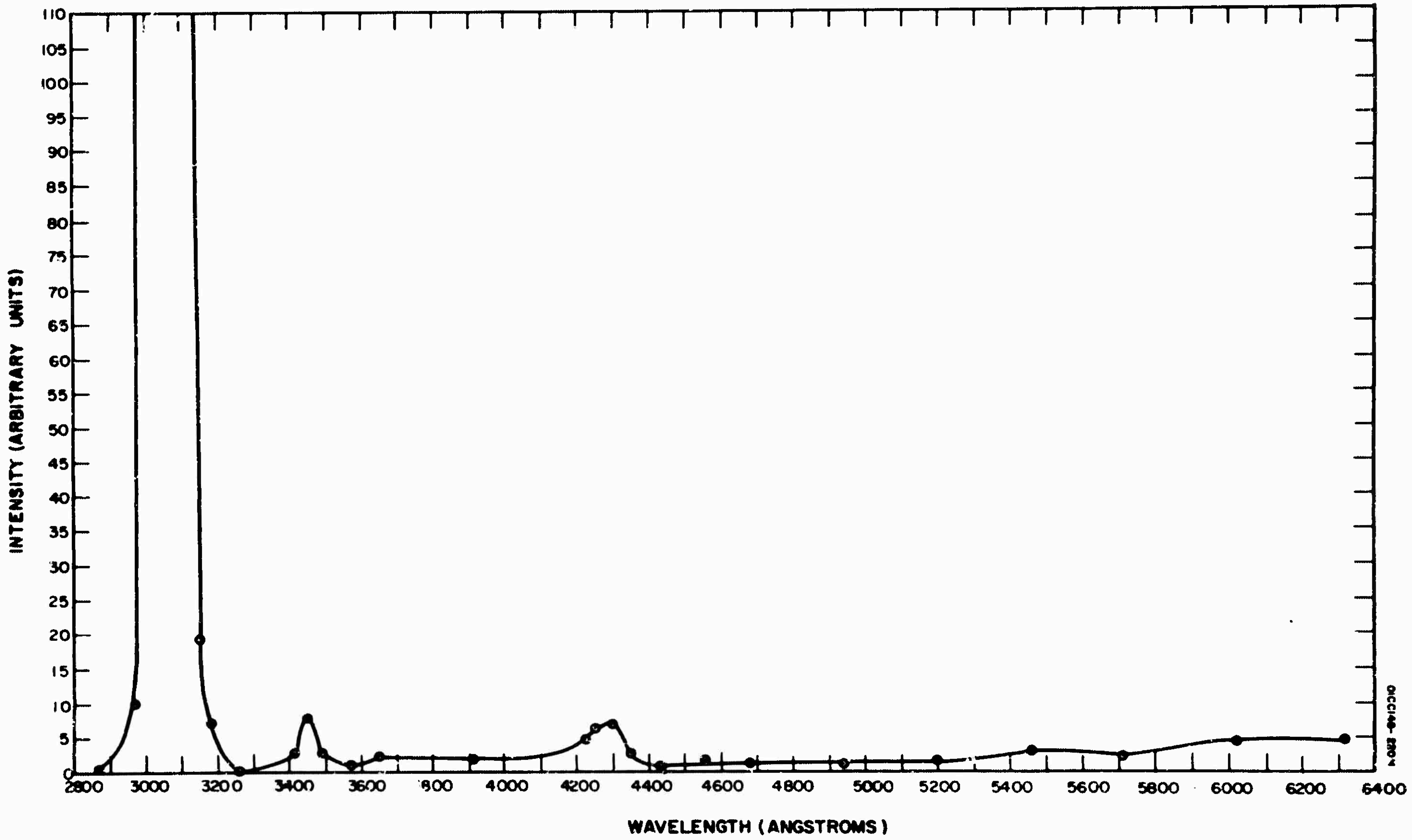

Figure 7. Relative intensity distribution of emission occurring in the reaction of oxygen atoms with ethylene.

which showed a lesser decrease. The addition of carbon dioxide quenched both CH and OH emissions at approximately the same rates, which were approximately equal to the quenching rate of the CH when molecular oxygen was added. It was also found that the CH and OH bands were quenched at approximately the same rate on addition of varying amounts of nitric oxide which was approximately as efficient a quencher as molecular oxygen. The fact that only in the case of O_2 is the OH less preferentially quenched may be taken as evidence that there is some production of excited OH from the reaction, $O_2 + CH \rightarrow OH^* + CO$. It should be noted, however, that unlike the acetylene case we were unable to observe the CN bands upon addition of nitric oxide which somewhat weakens this argument. The major reaction leading to OH emission is evidently entirely different from the one involved in the acetylene case since it does not depend on the presence of molecular oxygen.

The rate of quenching by molecular oxygen of the CH band at 4300 Å was compared in the acetylene and ethylene cases. The flowrates of acetylene and ethylene were adjusted and the atomic oxygen flowrate was maintained at a constant value such that, in the absence of molecular oxygen, the CH emission had equal intensity in each case. Various amounts of molecular oxygen were added and the decrease in emission from the CH was measured. The results are shown in Figure 8. It may be seen from this figure that the CH emission from the acetylene reaction is quenched much more readily

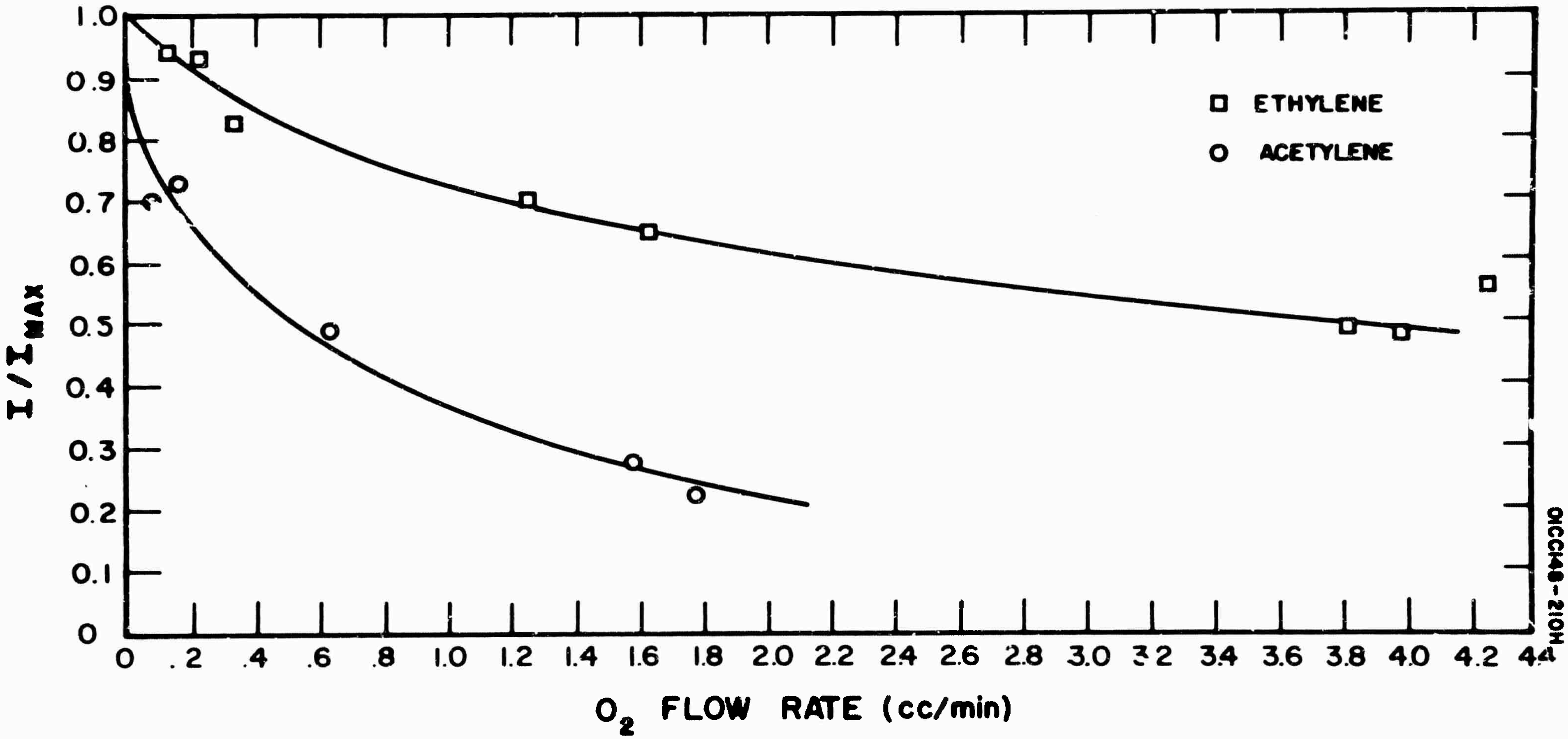

Figure 8. Effect of oxygen in quenching the CH emission occurring in the reactions of oxygen atoms with ethylene and acetylene.

than in the ethylene case. Since it is believed that the quenching action of O_2 in the acetylene case is really the attack of molecular oxygen on a free radical precursor and since it seems that both free radical scavenger and "inert" gases quench approximately equally in the ethylene case, the more rapid quenching of the acetylene CH compared with that of ethylene may be taken as evidence that collisional quenching is the dominant removal mechanism in the ethylene quenching. This is indirect evidence that the 4300 Å CH emissions are the result of different secondary reactions in the two cases.

1.2.8 The Reaction of Atomic Oxygen with Methane. It was found that luminescence from this reaction was very much weaker than that from either of the unsaturated hydrocarbon reactions. Using the flowrates apparatus a two hour exposure was required to detect any emission at all. Under these conditions there seemed to be a slight emission at 3064 Å which was undoubtedly due to the OH radical. Heating the reaction to several hundred degrees centigrade seemed to increase the emission only slightly.

This reaction was not pursued since it was evident that it could not contribute significantly to missile launch chemiluminescence.

1.2 9 Chemiluminescence from the Reactions of Acetylene and Ethylene at Low Pressures. It would appear from the work described here that the 3064 Å band of the hydroxyl radical contributes significantly to the total emission in both the acetylene and ethylene reactions. It therefore seemed relevant to attempt to measure the proportion of radiation which is in this band and if possible to give a quantum yield for the over-all reactions. The low pressure apparatus was used in this study.

The quantum efficiency of the reaction of atomic oxygen with nitric oxide has been measured with a reasonable degree of accuracy.(4) It has recently been shown that the quantum efficiency of that reaction remains unchanged even down to pressures of 1 micron Hg.(5) It is therefore possible to make rough comparisons of the relative efficiencies for light emission of the reactions of acetylene and ethylene with atomic oxygen by comparing their light emissions with that of the atomic oxygen — nitric oxide reaction over the same wavelength range and under the same conditions. In practice there are several problems involved in the method. Ideally one needs a detector which has a uniform response over the entire wavelength range which is studied. This is not readily available but over the range 3000 - 6000 Å the 1P28 photomultiplier (S5 cathode) approximates to this. Hence, in this work, a 1P28 photomultiplier was used as the detector. The second difficulty is that the reactions of ethylene and acetylene with atomic oxygen are so fast that appreciable quantities of the atomic oxygen present in the reaction vessel are used up and after a certain point the light emission actually shows a decrease as the hydrocarbon partial pressure is increased. The reaction vessel we have used functions on the steady state stirred reactor principle. Hence in order to make the principle operable, the added partial pressures of hydrocarbon were very small.

Most of the experiments in this study were carried out in the pressure range 6-8 microns Hg. An attempt was made to work at somewhat higher pressures but this proved to be impracticable since increasing the pressure (which was effected by throtting the valve between the reaction vessel and the pumps) meant that the residence time of the species in the reactor was also increased. The reactions were so fast that this lead to a decrease in light emission as the amount of hydrocarbon added was increased.

Experiments were carried out for each gas in the complete absence of molecular oxygen (using the N + NO titration technique), the presence of a small quantity of molecular oxygen (using argon as the carrier gas) and with oxygen as the predominant third body. The total light emission over the region 2000 - 6000 Å was measured with the photomultiplier and microammeter. The radiation above 3300 Å was measured by inserting a short wavelength cut-off filter. This latter figure was corrected for transmission losses of the filter by use of the nitric oxide - atomic oxygen emission. This reaction gives no emission below 3300 Å and hence any difference between the readings obtained with and without the filter are due to transmission losses. Hence these losses may be allowed for in the hydrocarbon reactions by multiplying the hydrocarbon light emission obtained with the filter by the ratio of the nitric oxide light emission without filter and that with filter. The radiation below 3300 Å which is due predominantly to the OH band at 3064 Å is then obtained by subtraction of the reading obtained without filter and the corrected reading with filter.

In agreement with the flow tube work it was found that when small additions of molecular oxygen was made to atomic oxygen produced by the nitrogen atom titration technique there was an increase in the OH emission from the atomic oxygen — acetylene reaction but no such effect was noted for the atomic oxygen — ethylene reaction. The results of the experiments are shown in Table 1. It may be seen from this table that a higher proportion of the emission lies in the OH band for the ethylene reaction than for the corresponding acetylene one. This also is in agreement with the flow tube data. In the case where there is no molecular oxygen present the OH emission from the acetylene chemiluminescence is low. When the atomic oxygen and molecular oxygen are present in an approximately 1:4 ratio the OH is increased to up to 20% of the total. The percentage is not increased perceptibly when molecular oxygen is made the predominant third body. Our flow tube work showed that there

TABLE 1.

INTENSITY MEASUREMENTS OF CHEMILUMINESCENCE FROM THE REACTIONS OF ATOMIC OXYGEN WITH ACETYLENE AND ETHYLENE AT LOW PRESSURES

Pressure (microns Hg.)	Predominant Third Body	Acetylene		Ethylene		% Intensity contained in a acetylene OH band	% Intensity contained in ethylene OH band	Intensity of 0 + NO Reaction for NO flow of 1c.c/min (amps)
		Flow Rate (c.c./min)	Intensity (amps)	Flow Rate (c.c./min.)	Intensity (amps)			
8	N_2	1.0	$0.115x10^{-5}$	0.3	$0.16x10^{-7}$	Not measured	Not measured	$0.23x10^{-6}$
6.5	A	1.0	$0.21x10^{-5}$	0.3	$0.7x10^{-7}$	7	40	$0.42x10^{-6}$
6.5	O_2	1.0	$0.42x10^{-5}$	0.3	$0.14x10^{-6}$	20	25	$0.9x10^{-6}$
14.5	N_2	1.0	$1.1x10^{-5}$	0.3	-----	0	--	$0.24x10^{-5}$
6.2	N_2	1.0	$0.89x10^{-6}$	0.3	$0.8x10^{-7}$	14	30	$0.34x10^{-6}$
6.2	A	1.0	$0.105x10^{-5}$	0.3	$0.6x10^{-7}$	22	40	$0.34x10^{-6}$

was negligible OH emission when molecular oxygen was absent. Hence it is likely that these readings are high owing to contributions from the CH band at 3300 Å and possibly weak continuous emission. However it is doubtful whether these errors contribute more than 50% of the total reading. The ethylene case is somewhat different in that molecular oxygen does not seem to play an appreciable role in the OH emission. It seems fairly consistent that about 30% of the total emission lies in this band. It is also a somewhat more accurate value since there is less contribution from neighbouring emission systems. It is probably fair to say that under upper atmosphere conditions a conservative estimate for the percentage of the emission between 3000 and 6000 Å in the OH band is at least 5% for the acetylene reaction and at least 30% for the ethylene reaction. If we take the known value for the rate constant for light emission for the atomic oxygen - nitric oxide reaction of 1.7×10^{-17} cc. molecule^{-1} sec^{-1} over the range 3000 - 6200 Å we may make reasonable estimates for the hydrocarbon reactions. The acetylene light emission is about a factor of 5 greater than that of nitric oxide under the same conditions whilst the ethylene luminescence is consistently a factor of 2 less. This enables us to estimate the rate constant for light emission of the acetylene - atomic oxygen reaction as 10^{-16} cc. molecule^{-1} sec^{-1} and that of the ethylene reaction as 10^{-17} cc. molecule^{-1} sec^{-1}. Curiously, it would seem from the way that the light emission drops off as the hydrocarbon partial pressure is increased, that the over-all rate constant for the acetylene reaction is less than that of the ethylene reaction by perhaps as much as an order of magnitude. Under these conditions the nitric oxide - atomic oxygen reaction liberates 1 quanta approximately every 10^7 collisions. Hence we may estimate that the corresponding acetylene and ethylene reactions give one quanta in the OH 3064 Å band for each 5×10^8 collisions and each 2×10^7 collisions respectively. These estimates are made on the basis that the reactions are two body processes.

1.2.10 Measurement of Atomic Oxygen Partial Pressure at Low Total Pressures. The nitrogen dioxide titration technique and variations of the method have been shown to be accurate for measuring oxygen atom concentrations in flow systems in the 1 mm pressure range. Nitric oxide is produced by the rapid reaction

$$O + NO_2 \xrightarrow{k_1} NO + O_2$$

and light emission occurs as a result of the much slower process

$$O + NO + M \xrightarrow{k_2} NO_2 + M + h\nu \ .$$

It has further been shown that there is maximum light emission when $[O] = 2[NO_2]$ and no light emission when $[O] = [NO_2]$.

At the low pressures prevailing in the stirred reaction difficulties were experienced using this method, because reaction (1) does not necessarily go to completion within the time periods available. Accordingly, a modification of the titration technique had to be worked out. This procedure and its implication was described in full in the semi-annual report dated 20 January 1964. A by-product of this study was the determination of the rate constant associated with reaction (1). A value of $2.5 \times 10^{-12} \pm 0.6$ cc/molecule sec was determined, from the extent of the asymmetry observed in the titration curve. This is in good agreement with that obtained by mass spectrometric methods.(6)

1.2.11 The Chemiluminescence of Atomic Oxygen and Carbon Monoxide at Low Pressures. Carbon monoxide is one of the most abundant by-products during a missile launch. Since it is known that carbon monoxide reacts with atomic oxygen to give light emission it seemed necessary to investigate the reaction at pressures which are comparable with those in the 90 km region of the atmosphere. Previous studies were made in the 1 min. pressure region and the results of the various workers are not in complete agreement. A major portion of the obtained results were presented in the semi-annual report dated 20 January 1964. These results can be summarized as follows: (a) under the low resolution employed, the emission appeared to be continuous, (b) the intensity of the emission is proportional to the oxygen atom concentration, (3) it is also proportional to the concentration of carbon monoxide, but independent on the total pressure. In the experimental results reported below will show, however, that although there is no dependence on pressure, the emission intensity varies with the nature of the main gaseous constitutent present; i.e., on the nature of the third body. The various findings will be discussed in the light of results obtained by other workers.

The recent experiments were performed using the low pressure apparatus with flowrates of 60 cc/min. Working in the region 10 - 60 microns Hg it was again found that the light emission was independent of pressure and directly proportional to the partial pressures of atomic oxygen and carbon monoxide. We then attempted to determine the effect of various third bodies. There is a fundamental difficulty involved at these low pressures in making absolute measurements of partial pressures. We have established that one is no longer in the viscous flow region but in the intermediate region between that and molecular flow. As such, one is not strictly correct in calculating the various partial pressures according to the ratio of the flowrates since the lighter gases are pumped faster than the heavier gases. However if we restrict our attention to nitrogen, argon and oxygen as the third bodies then the corrections do not exceed 10% since atomic oxygen will be pumped as the molecular species. A correction may be made for the effect of non-equal pumping after measuring directly the pressure due to specific flowrates of gases and added carbon monoxide. This procedure was adopted. The atomic oxygen flowrate was measured by titrating with nitrogen dioxide and matching the maximum glow with one produced by nitric oxide alone has been described earlier. This partial pressure of nitric oxide was also corrected. In this manner it was possible to measure I_o for both the nitric oxide — atomic oxygen reaction and the carbon monoxide — atomic oxygen reaction. The results are shown in Table 2. As may be seen from this table, there is an apparent dependence on the nature of the third body. One has to exercise caution in stating this since the differences are very small. However it is of some comfort to note that the $(I_o)_{NO}$ values are in excellent agreement with those obtained by Kaufman in the mm. region(7) The ratio of the $(I_o)_{NO}$ to $(I_o)_{CO}$ values are in reasonable agreement with those of Clyne and Thrush.(8) It therefore seems apparent that the mechanism which operates in the 1 mm. region is also the prevailing one at pressures as low as 10 microns.

Rate Constant for Light Emission.

It is possible to use the above data to make a reasonable estimate for the rate constant for light emission of the atomic oxygen — carbon monoxide reaction. It is known that over the range 3000 - 6200 Å the rate constant for light emission from O + NO is 1.7×10^{-17} cc/molecule^{-1} sec^{-1}. If we were able to obtain a photomultiplier with a "flat" response over this entire region then a direct comparison of the reaction rates could be made. Unfortunately,

TABLE 2. Values for Light Emission for Different Third Bodies

Third Body	$(I_o)_{NO}$ x 10^4 amps.	$(I_o)_{CO}$ x 10^8 amps.	$(I_o)_{NO}/(I_o)_{CO}$	$(I_o)NO$ Arbitrary Units (Kaufman 7)	$(I_o)_{NO}/(I_o)_{CO}$ (Clyne and Thrush 8)
O_2	0.20	0.60	3327	6.4	3300
A	0.24	0.73	3347	6.7	5000
N_2	.27	0.74	3593	7.3	--

the photomultiplier response falls off rapidly above 5000 Å and is down by a factor of four at 6000 Å. Little emission can be observed at longer wavelengths. Hence, under our conditions a better value for the rate constant would probably be 1.0×10^{-17} cc/molecule^{-1}sec^{-1}. This conclusion was reached from a study of the spectral distribution over the range 3000 - 6200 Å. Below 5000 Å in the "flat response" region the light emission is proportional to approximately 5000. Between 5000 Å and 6200 Å the light emission is proportional to approximately 18000 but this would be reduced to 9000 as a result of the lower sensitivity of the photomultiplier. Hence, the effective rate constant for light emission is

$$\left(\frac{5000 + 9000}{5000 + 18000}\right) 1.7 \times 10^{-17} \text{cc/molecule}^{-1}\text{sec}^{-1} = 1.0 \times 10^{-17} \text{cc/molecul}^{-1}\text{sec}^{-1}.$$

The carbon monoxide emission has a maximum intensity in the "flat response" region and can be compared directly. It was found that the ratio of $I_{o(NO)}/I_{o(CO)} \approx 3300$, in reasonable agreement with that found by Clyne and Thrush.(8) This gives us an over-all rate constant for light emission of

$$\frac{1}{3300} \times 10^{-17} = 3.0 \times 10^{-21} \text{ cc/molecule}^{-1}\text{sec}^{-1}$$

which is not likely to be in error by more than 50%.

1.3 DISCUSSION OF RESULTS

1.3.1 Discussion of Results Pertaining to O-CO Chemiluminescence.

In order to discuss and interpret the results which we have obtained, it is necessary, as a first step, to understand the results and interpretations of the other workers.(8,9) At this point, therefore, we will give a full account of their observations and what their interpretations entail.

1.3.2 Results of Clyne and Thrush.(8)

Their results are similar to ours although carried out in the 1 mm pressure region. The mechanism which they propose to account for their observations is given below.

Stabilization and Redissociation

$$O + CO + M \underset{k_{-1v}}{\overset{k_{1v}}{\rightleftarrows}} CO^*_{2(v)} + M \quad . \tag{1}$$

Vibrational Energy Transfer

$$CO^*_{2(v)} + M \underset{k_{v',v}}{\overset{k_{v,v'}}{\rightleftarrows}} CO^*_{2(v')} + M \quad . \tag{2}$$

Radiation

$$CO^*_2 \xrightarrow{k_{3v}} CO_2 + h\nu \tag{3}$$

Collisional Electronic Quenching

$$CO^*_{2(v)} + M \xrightarrow{k_{4v}} CO_2 + M \quad . \tag{4}$$

Applying a steady state treatment we get:

$$\left[CO^*_2\right] = \frac{[M]\left(k_{1v}[CO][O] + \sum_{v'}{}_{,v}\left[CO^*_2\right]_{v'}\right)}{k_{3v} + [M]\left(k_{-1v} + k_{4v} + \sum_{v} k_{v,v'}\right)} \tag{A}$$

The total emission is given by

$$I = \sum_{v} k_{3v} \left[CO_2^* \right]_v \quad .$$

Rate of formation of CO_2 is given by

$$\frac{d\left[CO_2 \right]}{dt} = \sum_{v} \left(k_{3v} + k_{4v} \quad [M] \right) \left[CO_2^* \right]_v \quad .$$

Now if k_{3v} << than all other terms in the denominator of Equation (A), then the observed I depends on the nature of M but not on the pressure of the carrier gas.

However, if this is the case, then the rate of formation of carbon dioxide is dependent upon M; this is in disagreement with the results of Mahan and Solo.(9)

The over-all combination reaction is spin forbidden,

$$CO\left({}^{1}\Sigma^{+}\right) + O\left({}^{3}P\right) \rightarrow CO_2\left({}^{1}{}_{g}\right)$$

Spin reversal occurs either:

(1) in the stabilization of a CO_2 molecule by a third body. This, it is claimed, would yield an increased intensity when oxygen is the major third body since oxygen (which has a triplet ground state ${}^{3}\Sigma_{g}^{-}$) would vacilitate spin reversal. On the other hand, it might be argued that the CO_2 would not be produced in an excited state and, if it were, then the molecular oxygen might be a more efficient quencher of the excited species to the ground state than, say argon.

(2) in the radiationless transition between two states before or after radiation. This transition could occur before or after the emission process; however, if it occurs after emission, it implies the presence of a very low-lying triplet state for CO_2, since the emitting state cannot lie more than 130 kcal/mole above the ground state of CO_2 and emission is observed below 3000Å (95 kcal/mole). No low-lying singlet or triplet state of CO_2 has been detected spectroscopically and none is expected. Clyne and Thrush, therefore, concluded that the emission is a singlet-singlet transition to the ground state of CO_2 and that spin reversal occurs in the radiationless transition between two excited states before emission.

(3) in the radiative process. This, however, would be expected to decrease I by accelerating the rate of quenching of triplet CO_2 molecules relative to the rate of emission.

Hence, Clyne and Thrush favor the second explanation given below. However, if one accepts all the data in the Mahan and Solo paper, then this mechanism cannot be correct since the rate of production of CO_2 would be dependent on the concentration of M unless the major portion of carbon dioxide is formed by an additional simple two-body process yielding CO_2 in the ground electronic state. It is also clear that in the low pressure region in which we have worked it is unlikely that $k_{9v} \ll$ the rest of the denominator of Equation (A) and hence the light emission should become three body dependent.

3.3 Results of Mahan and Solo.(9) These workers claim that an increase in the total pressure (over the range 0.56 to 1.9 mm Hg) decreases the quantum yield — the quantum yield is defined as the light emitted per unit amount of carbon dioxide. The data from which they draw this conclusion are reproduced in Table 3 . However, as can be seen from Figure 9 , the data can equally well show that the light emission is directly proportional to the amount of carbon dioxide produced. This would indicate that the light emission was not pressure dependent over the pressure range 0.56 to 1.9 mm of Hg. It is thought that, within these workers' probable limits of experimental uncertainty, this may be a legitimate straight line plot.

Further studies by these workers indicate that the light emission is quenched considerably by the addition of small quantities of molecular oxygen when the predominant third body was argon. This quenching was in apparent agreement with the Stern-Volmer quenching law. It was also found that small amounts of molecular oxygen increased the amount of carbon dioxide formed, indicating to them that there was a secondary reaction between the excited carbon dioxide and molecular oxygen, thus:

$$CO_2^{+} + O_2 \rightarrow CO_2 + 2O$$

and

$$CO_2^{*} + O_2 \rightarrow CO_2 + 2O$$

When the molecular oxygen reached a value of approximately 10% of the total amount of third body present, then the production of carbon dioxide became independent of the molecular oxygen.

TABLE 3

ABSOLUTE QUANTUM YIELDS* (MAHAN AND SOLO)

Run	CO	$O_2 \times 10$	Ar	$CO_2 \times 10^3$	Flow Rate	Pressure	$(\text{Quantum Yield})^{-1}$	Intensity
1A	0.27	0.39	0.25	0.82	20.9	0.56	500	164
1B	0.38	0.58	0.37	1.6	14.4	0.81	580	276
2A	0.75	0.34	0.20	0.65	34.4	0.98	480	135
2B	1.0	0.49	0.31	0.88	24.4	1.4	530	166
3A	1.34	1.6	0.41	0.37	17.9	1.9	780	47
3B	1.09	1.3	0.35	0.28	21.6	1.6	660	42

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* All quantities except Flow Rate, Quantum Yield and Intensity are in mm. Flowrate is in units of liters/min, Quantum Yield is the number of quanta emitted divided by the total number of carbon dioxide molecules produced, and the Intensity is in arbitrary units.

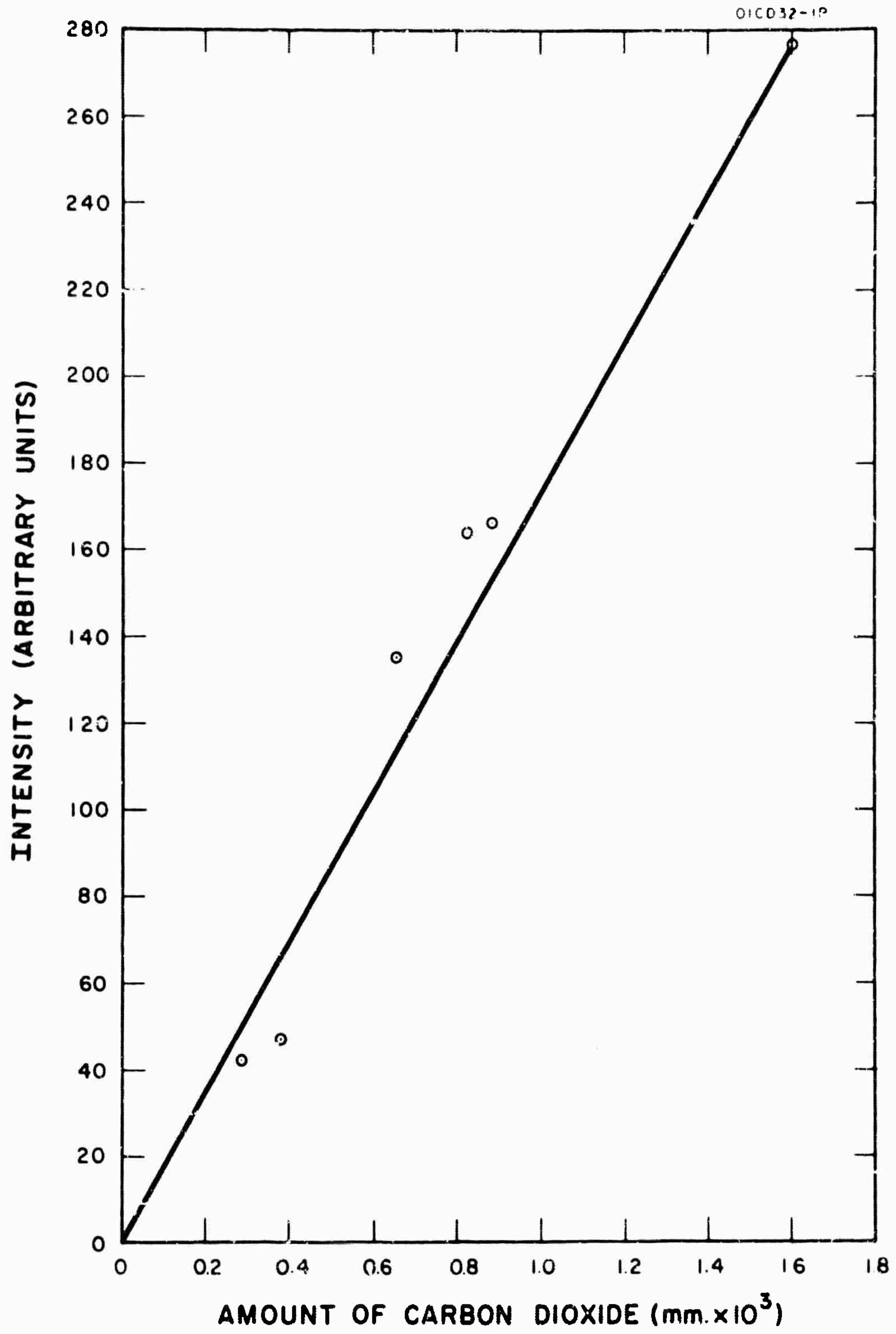


Figure 9. Intensity of light emission as function of carbon dioxide produced (data of Mahan & Solo)

It was found that the pressure range 0.18 to 1.44 mm, the rate of production of carbon dioxide was independent of the third boyd M. They, therefore, concluded that the over-all rate of production of CO_2 went according to the equation $d(CO_2)/dt = k(CO)(O)$.

The following mechanism was used by them to explain their results:

$$O + CO \rightarrow CO_2^+ \text{ nonradiative} \tag{5}$$

$$O + CO \rightarrow CO_2^* \text{ radiative} \tag{6}$$

$$CO_2^+ + M \rightarrow CO_2 + M \tag{7}$$

$$CO_2^* + M \rightarrow CO_2 + M \tag{8}$$

$$CO_2^* \rightarrow CO_2 + h\nu \tag{9}$$

$$\left[CO_2^+\right] = \frac{k_5[O][CO]}{k_7[M]}$$

$$\left[CO_2^*\right] = \frac{k_6[O][CO]}{k_8[M]+k_9}$$

$$\begin{aligned} d\left[CO_2\right]/dt &= k_7[M]\left[CO_2^+\right] + k_8[M]\left[CO_2^*\right] + k_9\left[CO_2^*\right] \\ &= k_5[O][CO] + \frac{k_6k_8[M][O][CO]}{k_8[M] + k_9} + \frac{k_6k_9[O][CO]}{k_8[M] + k_9} \\ &= k_5[O][CO] + \frac{k_6[O][CO]\left(k_8[M] + k_9\right)}{k_8[M] + k_9} \\ &= \left(k_5 + k_6\right)[O][CO] \end{aligned}$$

Hence, the rate of production of carbon dioxide is independent of M.

$$I = k_5\left[CO_2^*\right] = \frac{k_6k_9[O][CO]}{k_8[M] + k_9} \quad .$$

It can be seen that the light emission is dependent upon [M].

The above mechanism can explain all the results of Mahan and Solo; but as can be seen, it cannot be reconciled with the results of Clyne and Thrush or with our own results, since the light emission is dependent upon pressure. However, as we have shown, these results may also be interpreted as showing that the light emission is not pressure dependent. (See Figure 9.)

1.3.4 New Mechanism. We think it is therefore necessary to give a mechanism which will explain both our observations and those of the other two sets of workers. We attempt to do this with the following mechanism.

The over-all combination reaction is spin forbidden:

$$CO\left({}^1\Sigma^+\right) + O\left({}^3P\right) \rightarrow CO_2\left({}^1\Sigma_g^+\right) .$$

If, however, spin reversal occurs in the stabilization of the excited CO_2 molecules by a third body, then we might write the mechanism as

$$O + CO \rightarrow CO_2^+ \quad (10)$$

$$CO_2^+ \rightarrow O + CO \quad (11)$$

$$CO_2^+ + M \rightarrow CO_2^* + M \quad (12)$$

$$CO_2^* + M \rightarrow CO_2^+ + M \quad (13)$$

$$CO_2^* + M \rightarrow CO_2 + M \quad (14)$$

$$CO_2^+ + M \rightarrow CO_2 + M \qquad (15)$$

$$CO_2^* \rightarrow CO_2 + h\nu \qquad (16)$$

$$CO_2^+ \rightarrow CO_2 + h\nu \qquad (17)$$

If molecular oxygen is present in any significant amount, then reactions (12) and (15) are facilitated since the ground $\left({}^3\Sigma_g^-\right)$ state of oxygen would be expected to facilitate spin reversal. Hence, while it is possible for the stabilization to give CO_2 in an excited singlet state, as in reaction (12), it is also possible that reaction (15) will occur, which gives CO_2 in its ground singlet state. It would seem that the statement of Clyne and Thrush that the stabilization of the excited CO_2 molecule by molecular oxygen would lead to an increased I value is not necessarily correct since the "quenching" effect of reaction (15) would also become more evident. It might be argued also that it is difficult to avoid the molecular oxygen or the atomic oxygen playing a dominant part as the third body, since if it is only present in small quantities, then it might still be several orders of magnitude more efficient than an inert gas. Our results (i.e., the light emission is increased with argon as the apparent predominant third body) is, therefore, not in disagreement with this theory since reaction (15) would decrease at least in relation to reaction (12) even if atomic and molecular oxygen were not present in significant quantities.

It is necessary at this point to see if our mechanism will fit the observations of Mahan and Solo. These will be taken in turn.

(1) The absolute quantum yield decreases with pressure over the range 0.56 to 1.9 mm Hg. As we have shown in Figure 9, we believe that these results may be interpreted as showing that the quantum yield is independent of pressure. However, one can take another approach. The relative amount of molecular oxygen present in these workers' experiment (Table 3) varies from 3.5 to 8.4 percent. This is probably sufficient to make the molecular oxygen play a major role as the third body. It can be argued that even if one agrees that the quantum yield decreases, then from the limited amount of data available, if I is assumed constant, the amount of CO_2 formed increases as O_2 increases. This also would not be contradictory to our observations.

If we accept our observations that the light emission is independent of pressure, then our mechanism is consistent with this since in the steady state:

$$I = k_{16}[CO_2^*] + k_{17}[CO_2^+]$$

$$[CO_2^*] = \frac{k_{12}[M][CO_2^+]}{k_{13}[M] + k_{14}[M] + k_{16}}$$

$$[CO_2^+] = \frac{k_{10}[O][CO] + k_{13}[M][CO_2^*]}{k_{11} + k_{12}[M] + k_{15}[M] - k_{17}}$$

Substituting

$$[CO_2^+] = \frac{k_{10}[O][CO]\ (k_{13}[M] + k_{14}[M] - k_{16} + k_{12}\ k_{13}[M][M][CO_2^+]}{(k_{13}[M] + k_{14}[M] + k_{16})\ (k_{11} + k_{12}[M] + k_{15}[M] + k_{17})}$$

$$= \frac{k_{10}[O][CO]\ (k_{13}[M] + k_{14}[M] + k_{16})}{(k_{13}[M] + k_{14}[M] + k_{16})\ (k_{11} + k_{12}[M] + k_{15}[M] + k_{17}) - k_{12}k_{13}[M]^2}$$

$$[CO_2^*] = \frac{k_{10}k_{12}[O][CO][M]}{(k_{13}[M] + k_{14}[M] + k_{16})\ (k_{11} + k_{12}[M] + k_{15}[M] + k_{17}) - k_{12}k_{13}[M]^2}$$

$$I = \frac{k_{10}k_{12}k_{16}[O][CO][M] + k_{10}k_{17}\ [O][CO]\ (k_{13}[M] + k_{14}[M] + k_{16})}{(k_{13}[M] + k_{14}[M] + k_{16})\ (k_{11} + k_{12}[M] + k_{15}[M] + k_{17}) - k_{12}k_{13}[M]^2}$$

$$I = \frac{k_{10}[O][CO]\ (k_{12}k_{16}[M] + k_{17}(k_{13}[M] + k_{14}[M] + k_{16}))}{(k_{14}[M] + k_{16})\ (k_{11} + k_{17} + k_{12}[M] + k_{15}[M] + k_{13}[M]\ (k_{11} + k_{15}[M] + k_{17})}$$

k_{10} and k_{11} are unknown. k_{16} is an allowed transition $\sim 10^6 - 10^8$ sec^{-1}, deactivation by collision is expected to be an efficient process and hence it is assumed to occur at the collision frequency, i.e., $k_{12} = k_{13} = k_{14} = k_{15} = 10^{-10}$ cm^3 molecule^{-1} sec^{-1}.

Now at low pressures (say 1 micron hg.)

$$M = 3 \times 10^{13} \text{ molecules/cc}, \quad k_{16} >> k_{14}[M] + k_{13}[M]$$

$$I = \frac{k_{10}[O][CO]\ (k_{12}k_{16}[M] + k_{17}k_{16})}{k_{16}(k_{11} + k_{17} + M(k_{12} + k_{15}) + k_{13}[M]\ (k_{11} + k_{17} + k_{15}[M])}$$

Since k_{17} is not an allowed transition it is not unreasonable to assume a lifetime as long as 10^{-2} sec for it. Hence $k_{17} << k_{12}[M]$ and if k_{11} is small:

$$I = \frac{k_{10}k_{12}k_{16}[O][CO][M]}{k_{16}[M]\ (k_{12} + k_{15})}$$

i.e.,

$$I = \frac{k_{10}k_{12}[O][CO]}{(k_{12} + k_{15})}$$

That is, our mechanism suggests the light emission should be independent of pressure in the region 1 micron to 10 mm, and should vary inversely as the pressure above this. At low pressures the light emission would however be dependent on the nature of the third body, since k_{12} and k_{15} would vary with M.

(2) <u>The relative quantum yield decreases in apparent agreement with a Stern-Volmer quenching law as small amounts of molecular oxygen are added</u>. Again, it is noted that the molecular oxygen is never present in quantities of less than 1.5 percent and is gradually increased to 20 percent. Hence, in the reactions

$$CO_2^+ + O_2 \rightarrow CO_2^* + O_2 \qquad (18)$$

$$CO_2^+ + O_2 \rightarrow CO_2 + O_2 \qquad (19)$$

somewhat more of the CO_2^+ may be preferentially placed in a nonexcited singlet state.

(3) <u>Small amounts of molecular oxygen increase the amount of carbon dioxide formed</u>. This is interpreted by Mahan and Solo as evidence for the chain-branching mechanism

$$O_2 + CO_2^+ \rightarrow CO_2 + 2O$$

$$O_2 + CO_2^* \rightarrow CO_2 + 2O$$

It may not be necessary to postulate this explanation, however. We can again argue that on our mechanism the addition of small amounts of of molecular oxygen will increase the degree of importance of reactions (18) and (19), and hence by the arguments given in the previous paragraph the required increase in CO_2 would be produced.

(4) The reaction is first order with respect to both oxygen atoms and carbon monoxide, but zero order with respect to total pressure. Our mechanism yields the following expression for the production of carbon dioxide:

$$d(CO_2)/dt = k_{14}[M][CO_2^*] + k_{15}[M][CO_2^+] + k_{16}[CO_2^*] + k_{11}[CO_2^+]$$

$$= [CO_2^*]\ (k_{16} + k_{14}[M]) + [CO_2^+]\ (k_{17} + k_{15}[M])$$

At low pressures $k_{16} \gg k_{14}[M]$ and $k_{17} \ll k_{15}[M]$

$$d(CO_2)/dt = k_{16}(CO_2^*) + k_{15}[M][CO_2^+]$$

$$= \frac{k_{16}k_{10}k_{12}[O][CO][M] + k_{15}[M]\ k_{10}[O][CO]\ (k_{13}[M] + k_{14}[M] + k_{16})}{(k_{13}[M] + k_{14}[M] + k_{16})\ (k_{11} + k_{12}[M] + k_{15}[M] + k_{17}) - k_{12}k_{13}[M]^2}$$

$$= k_{10}[O][CO]$$

The rate of production of carbon dioxide is independent of M provided that any additional carbon dioxide is formed in a non-radiative state by a simple two body process. Hence our mechanism does not conflict with the data of Mahan and Sato in this respect.

1.3.5 Conclusions. It is interesting to note that ours is the third mechanism to be proposed for this reaction. However it is capable of being reconciled with all of the experimental data. It is difficult to interpret our data or pressures as low as 10 microns on any other mechanism since there is an apparent nature of the third body dependence which is not compatible with the Mahan and Salo scheme and the light emission is independent of pressures which should not be the case with the Clyne-Thrush mechanism at pressures much below 1 mm. It seems evident that the same mechanism must be proposed for the 1 mm data and for our low pressure results since the ratio of (I_o) and $(I_o)_{CO}$ found by ourselves and Clyne and Thrush are in good agreement. Also it seems that there is no fall-off in the $(I_o)_{NO}$ at pressures down to 1 micron.(5)

This mechanism may be applied with only slight modification to account for the light emission from the atomic oxygen - nitric oxide reaction. The original mechanism proposed(10) suffers from the difficulty that it predicts the light emission should become pressure dependent in the 10 micron region and also that the light emission should arise from two electronic states since the lifetimes of the states suggested are sufficiently close that neither should be neglected.(11) Since we have shown(5) that the light emission does not become pressure dependent at pressures as low as 1 micron, it is interesting to note that this mechanism provides a possible explanation. It has been suggested that initially the nitrogen dioxide is formed in a high vibrational level of the ground electronic state and then is transferred with the excited electronic state from which it emits.(12) If this suggestion is correct then we may use our mechanism where NO_2^+ is the vibrationally excited ground electronic state. The lifetime of this is anticipated to be of the order of 10^{-2} sec and hence identical arguments to those forwarded for the carbon monoxide reaction may apply.

The conclusion from the present study is however that the reaction of atomic oxygen with carbon monoxide cannot contribute significantly to the chemiluminescence during missile launches owing to its low rate constant for light emission of 3×10^{-21} cc molecule^{-1} sec^{-1}.

SECTION 2

MASS SPECTROMETER STUDIES

2.1 INTRODUCTION

The principal objective of this part of the experimental program was to investigate chemiluminescent reactions with respect to their kinetic mechanisms, placing specific emphasis upon the determination of the initiation reactions and the associated rate constants. For this purpose an apparatus incorporating a mass spectrometer attached to a flow reactor had been constructed under the previous contract. During the period covered by the present contract, the mass spectrometer was further improved, and a series of investigations carried out on reactions involving atomic oxygen. Specifically, the reactions of oxygen atoms with acetylene, ethylene and carbonyl sulfide were studied. A major portion of the results obtained were presented in the two semi-annual reports issued during the last year.

2.2 APPARATUS

A detailed description of the mass spectrometer construction and associated equipment was given in the Final Report on Contract No.

AF19(628)-231, and improvements were described in the first Semi-Annual Report dated 20 January 1964 under the present contract. The principle experimental arrangement is sketched in Figure 10. A measured flow of dried oxygen was passed through a microwave-powered discharge producing about 5% dissociation, before entering the reactor. (Other methods of producing oxygen atoms are described in the subsequent section.) The other reactant was fed into the partially dissociated O_2 flow via a multi-hole jet inlet with the holes being directed perpendicular to the main gas stream in order to ensure good mixing. The jet head could be moved along the axis of the reactor so that the duration of the reaction was controlled by the distance from the MS sampling orifice.

The MS ion source was designed to minimize wall collisions thus favoring the detection of free radicals. The central portion of the broad molecular beam developing at the sampling orifice was directed into the porthole of a moderately fast diffusion pump, traversing the ionization region on its way. The relatively large openings required in the ionization box were fitted with 90% transparent screens and guard rings which prevented excessive field penetration. It was also found necessary to cover the outside surface of the reactor opposite the ionization box with a metallic shield in order to eliminate perturbing charge-up effects. A system of cylinder lenses focussed the resulting ions onto the entrance aperture of a 60 degree mass analyzer employing a permanent magnet. The mass range covered by variation of the ion acceleration voltage extended from mass 12 to mass 65 with an observed

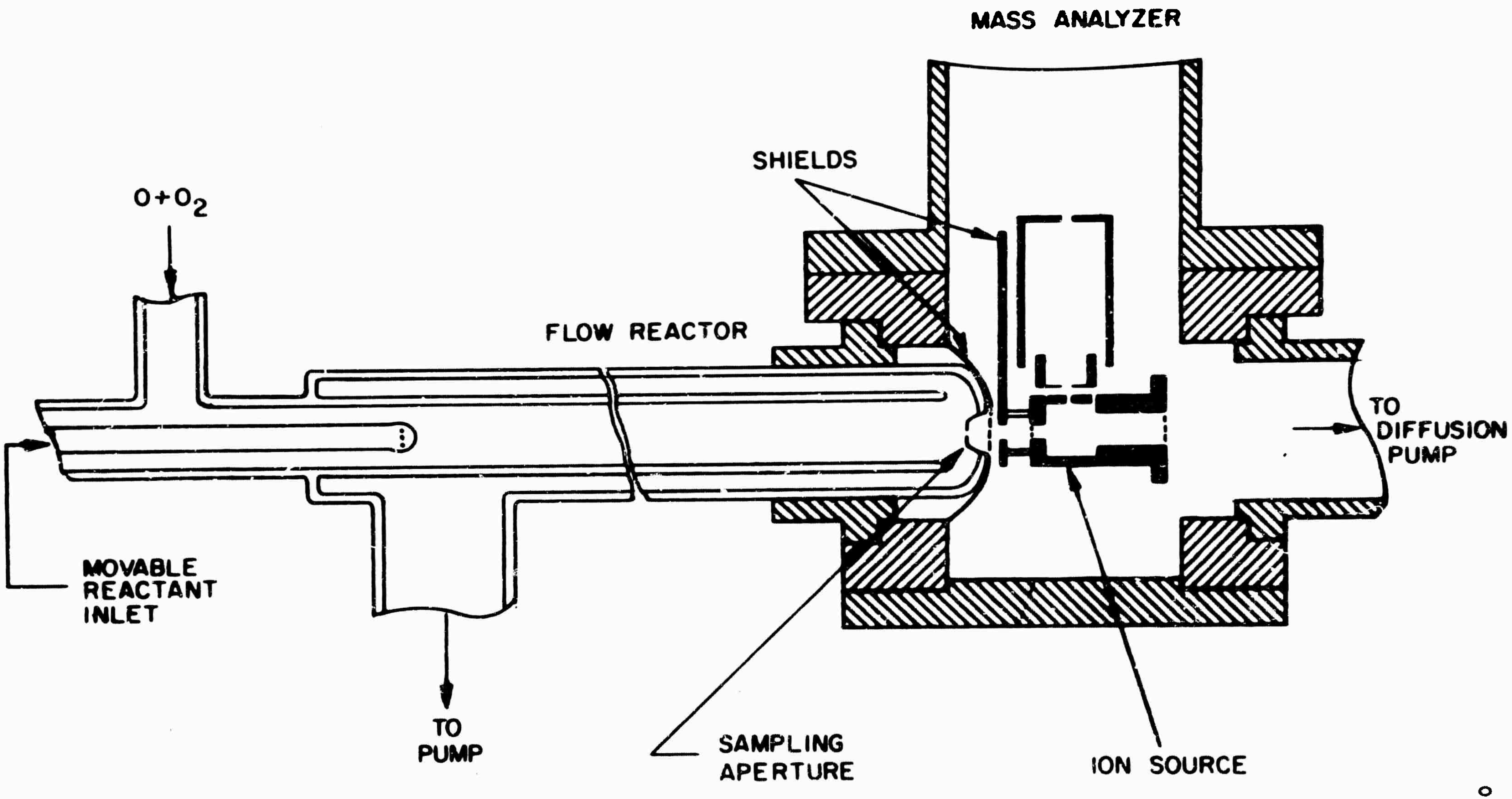


Figure 10. Apparatus for the study of atom reactions.

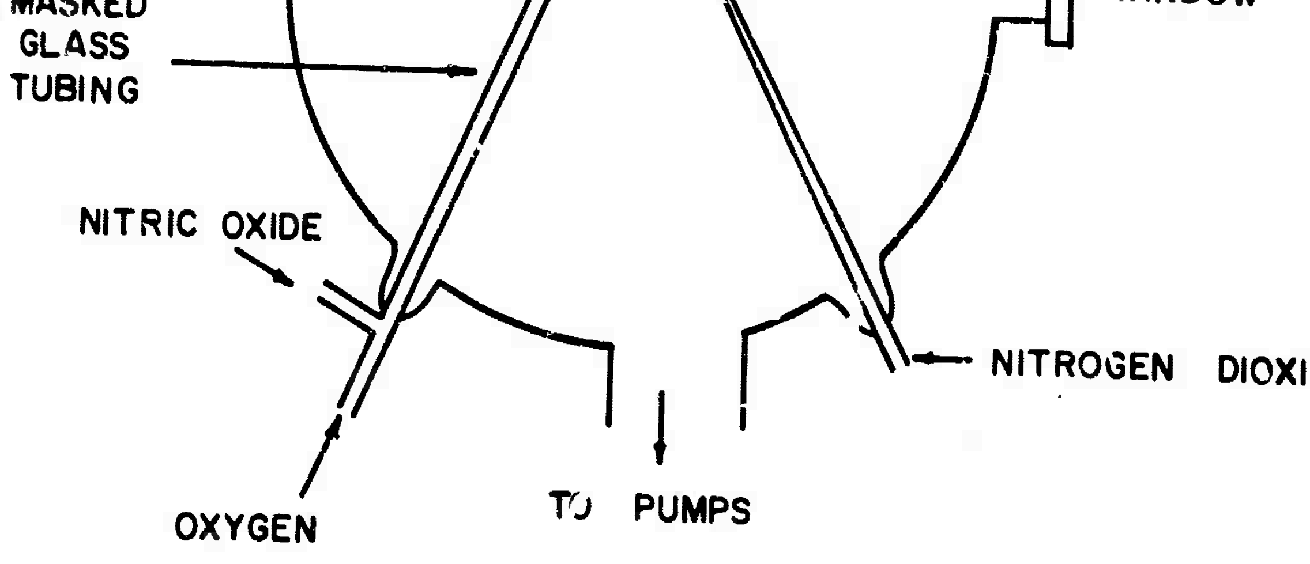


Figure 2. Diagram of low pressure reaction cell.

speed. The spectra were recorded using a Leeds and Northrup 10 millivolt recorder. The detector used was an E.M.I. 9558B photomultiplier tube fitted with a quartz window and was designed for use in the region 2500 to 7500 Å. A special preamplifier was used to minimize electrical pick-up.

On occasion, particularly with the low pressure apparatus, it was desirable to measure the intensity of the over-all light emission. These measurements were made with either a RCA 1P28 photomultiplier (S5 cathode) or EMI 9558B photomultiplier (S20 cathode) coupled to

carried out in the presence of large quantities of molecular oxygen, it was one of the aims of the present study to investigate the reaction in the absence of molecular oxygen and to determine the effect of O_2 on the light emission. As was mentioned earlier, this was accomplished by discharging a 99:1 ratio of argon and oxygen or by making the oxygen atoms by titrating atomic nitrogen with nitric oxide. Most of the results were described in detail in the semi-annual report under this contract dated 20 January 1964, and 20 July 1964. Hence, it suffices to give a brief summary here.

4300 Å were formed from the same reactions at the same rate. Similarly, it is suggested that the C_2 bands are formed predominantly by one reaction.

The addition of molecular oxygen upstream of the mixing region had two effects: (a) the C_2 bands, the CH bands and the continuum were strongly quenched and (b) the OH system at 3064 Å became evident. A typical plot of the data is shown in Figure 3b which is the sister graph of Figure 3a. It is seen that the maximum excited OH is formed at a time between that of C_2 and the emitter of the

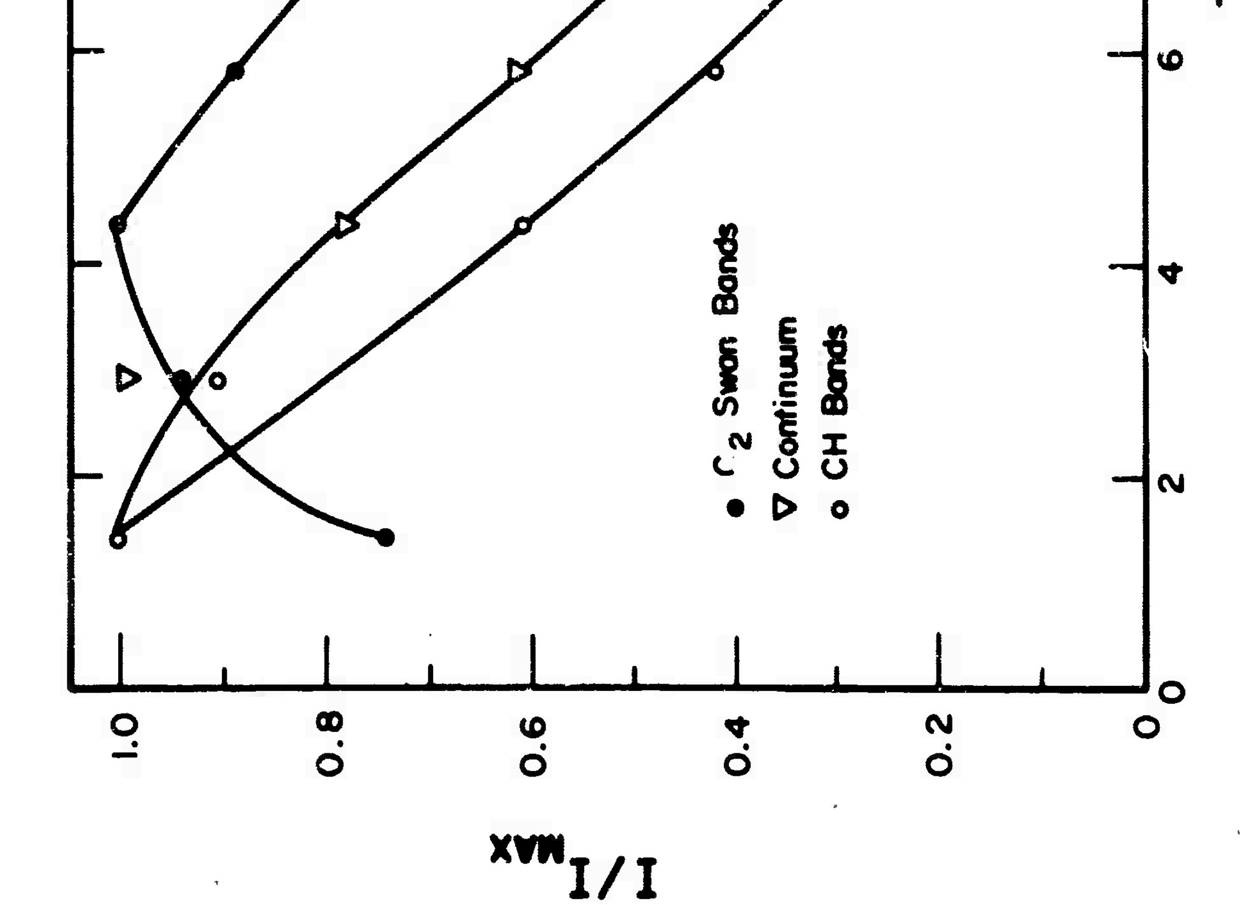


Figure 3a. Reaction of acety
formation of emit

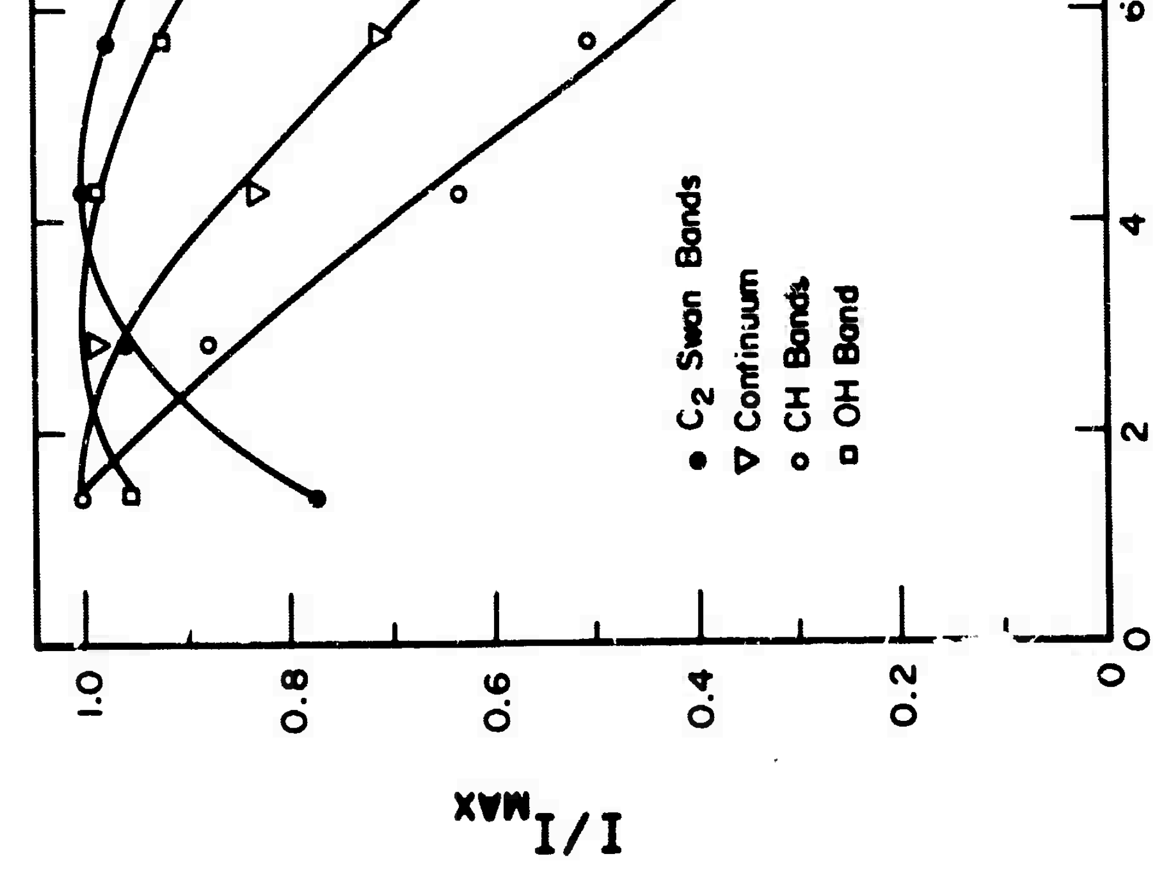
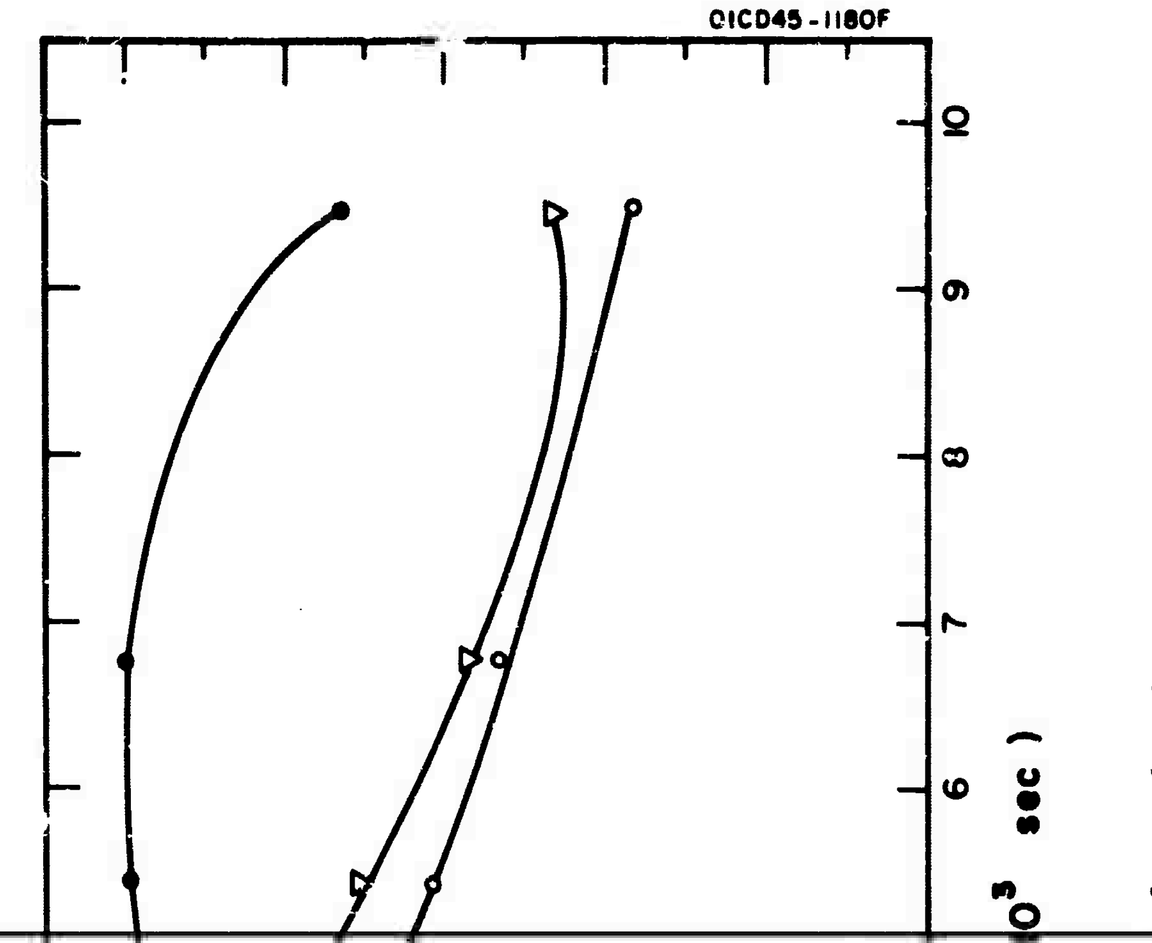


Figure 3b. Reaction of ac
formation of e

is not). Additions of each gas were made
approximately 2% of the total flow and th
bands was measured. It was found that ca
slight quenching effect which was of the
and nitric oxide were both very efficient
efficiency of nitric oxide as a quencher
should be noted that in addition to its
oxide gives rise to CN and NH bands at 3
investigation of the relationship has be
cations were discussed in a previous rep



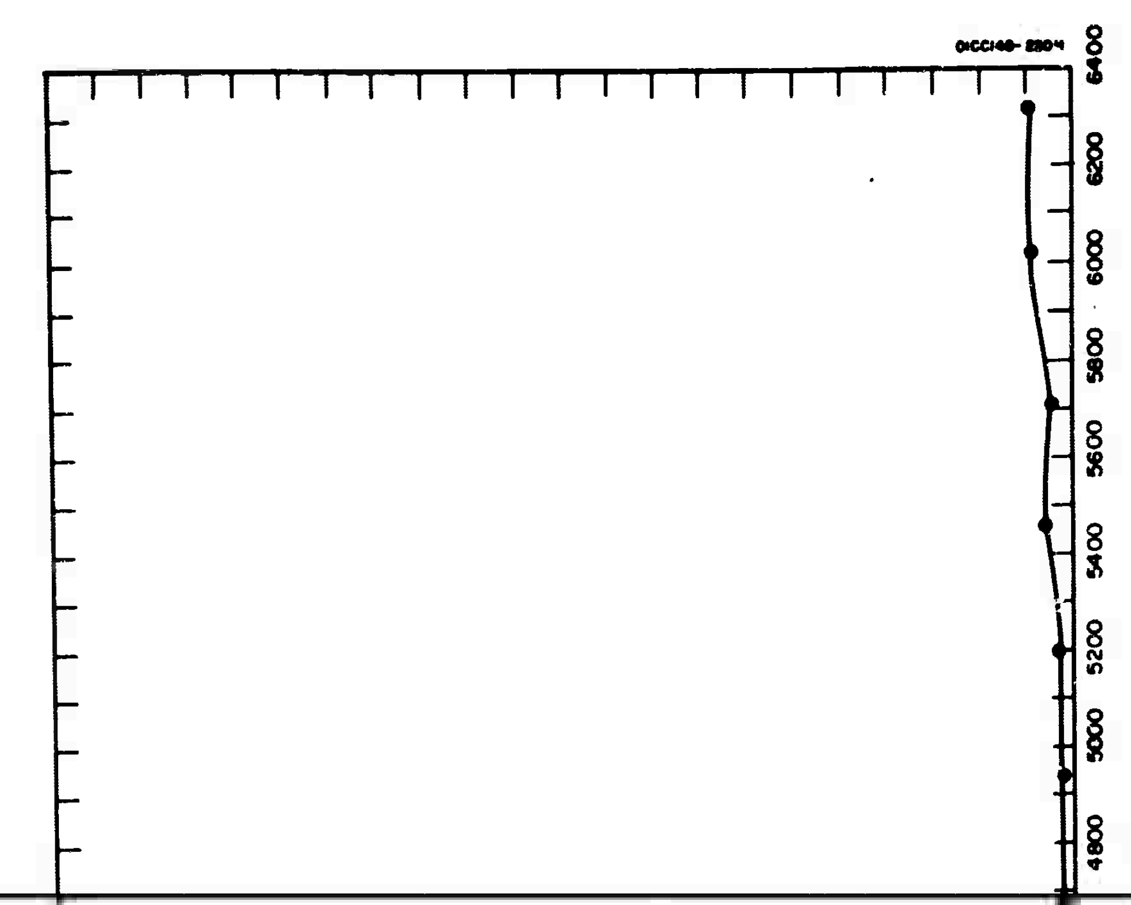
of acetylene by argon as a function of time.

does not contain oxygen and, hence, the likely emitter is a fragment of the acetylene molecule itself.

1.2.5 Spectral Distribution of the $O + C_2H_2$ Chemiluminescence. In these experiments the spectra obtained were corrected for the spectral response of the instrument. The spectrometer was first calibrated over the spectral region 3600 Å to 7000 Å using a stable source of known flux and spectral distribution. This source which was a tungsten ribbon filament lamp had itself been calibrated by a N.B.S. standard light source. A check on our calibration was made by recording the spectrum of the atomic oxygen — nitric oxide light emission over this wavelength region. The spectral intensity at various wavelengths was corrected by multiplying by the ratio

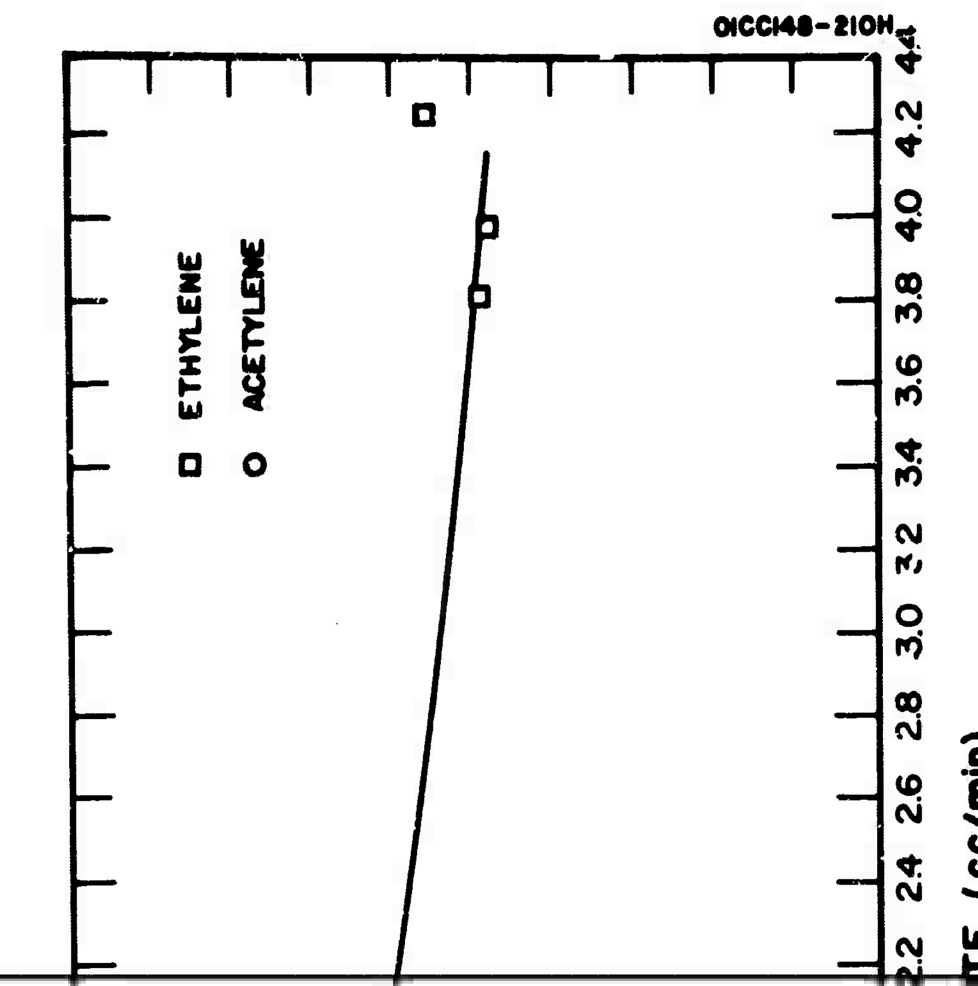
1.2.6 Infrared Radiation. A qualitative investigation was undertaken to examine the possibility that the reaction of acetylene with atomic oxygen produced significant vibrational excitation and hence infrared radiation. A lead sulfide detector was used and any signals were detected on an oscilloscope. It was found that the reaction gave significant radiation even beyond 2 microns. No attempt was made to identify the emitter or emitters but this is obviously in the fundamental frequency range and one can tentatively suggest carbon monoxide as a likely source.

1.2.7 The Reaction of Atomic Oxygen with Ethylene. The light emission produced by the reaction of atomic oxygen with ethylene is well known to be considerably less than that from the corresponding



ribution of emission occurring
en atoms with ethylene.

which showed a lesser decrease. The addition of carbon dioxide quenched both CH and OH emissions at approximately the same rates, which were approximately equal to the quenching rate of the CH when molecular oxygen was added. It was also found that the CH and OH bands were quenched at approximately the same rate on addition of varying amounts of nitric oxide which was approximately as efficient a quencher as molecular oxygen. The fact that only in the case of O_2 is the OH less preferentially quenched may be taken as evidence that there is some production of excited OH from the reaction, $O_2 + CH \rightarrow OH^* + CO$. It should be noted, however, that unlike the acetylene case we were unable to observe the CN bands upon addition of nitric oxide which somewhat weakens this argument. The major reaction leading to OH emission is evidently entirely



ng the CH emission occurring in the
th ethylene and acetylene.

than in the ethylene case. Since it is
action of O_2 in the acetylene case is re
oxygen on a free radical precursor and s
free radical scavenger and "inert" gases
equally in the ethylene case, the more r
acetylene CH compared with that of ethyl
that collisional quenching is the domina
ethylene quenching. This is indirect ev
CH emissions are the result of different
two cases.

1.2.8 The Reaction of Atomic Oxyge
found that luminescence from this reacti

resolution of about $M/\Delta M = 30$. This was sufficient for the present work. Rhenium filaments were found to be most suitable to withstand the rather severe conditions imposed by the strongly oxidizing atmosphere. MS sensitivities for the various constituents were determined before and after a series of runs. For this purpose, the reactor was filled with the desired gas, the static pressure measured with a McLeod gauge, or a CEC Diaphragm Manometer and the signal strength at the pertinent mass number recorded. In addition, the signal strength on all mass numbers was checked repeatedly for each run.

2.2.2 Oxygen Atom Concentration Measurements.

Oxygen atoms were produced by three different methods: (a) by discharging tank oxygen (b) by the use of a helium-oxygen mixture instead of pure oxygen to reduce the O_2 partial pressure to less than ten percent of the total pressure, and (c) by discharging nitrogen and adding sufficient amounts of NO behind the discharge to convert the resulting N atoms quantitatively into oxygen atoms by virtue of the fast reaction $N + NO \rightarrow N_2 + O$. This latter method gave O-atoms in the presence of N_2 with molecular oxygen virtually absent.

Using discharged tank oxygen, the initial oxygen atom concentration was determined by two independent procedures: (a) from the decrease of the mass 32 signal when the discharge was excited and (b) by means of the NO_2 "clean up" method which utilizes reaction (3). In case (a) it was assumed that oxygen atom recombination within the MS ion source is negligible. The oxygen atom pressure is then given by

$$P_a = \frac{2\Delta H(32)}{S(32)}$$

where $\Delta H(32)$ is the recorded change in peak height at mass number 32 while S(32) is the corresponding sensitivity for molecular oxygen. Method (b) assumes that reaction (3) is essentially completed before sampling becomes effective, so that the consumption of NO_2 which is admixed in excess represents the available oxygen atom concentration. The loss of NO_2 was measured by the decrease of the signal at mass number 46. Both methods gave substantially identical results which indicates that the effect of oxygen atom recombination in the MS ion source is indeed negligible. With helium-oxygen mixtures the initial oxygen atom concentration was determined from the decrease of the O_2 parent peak at mass number 32. When oxygen atoms were produced from the reaction of nitrogen atoms with NO, the initial oxygen atom concentration was deduced from the consumption of nitric oxide. In the latter two cases, it was possible to monitor the oxygen atom concentration by means of the contribution to the mass 16 peak. The sensitivity of atomic oxygen on mass number 16 was determined from the observed contribution to the signal on this mass number in the absence of other reactants.

2.3 OBSERVATIONS

2.3.1 Acetylene. Upon the admixture of acetylene to a flow containing oxygen atoms, the occurrence of a reaction was indicated by the well known chemiluminescence associated with the oxygen atom-acetylene reaction. The glow was observed to fill the entire reactor tube downstream of the mixing point. The major products observed were carbon monoxide water vapor and hydrogen. However, no quantitative measurements were made concerning hydrogen due to the somewhat erratic behavior of the respective signal which is still not interpreted. Likewise, the signals observed on mass 17 and 18 which are due to water vapor has not yet been analyzed in a quantitative manner. A contribution to the mass 12 peak was observed to occur under all investigated conditions. The size of the signal was beyond that to be expected from the fragmentation of CO. If taken at face value, this would imply the presence of carbon stoms, but a contribution to the signal on mass 12 could also originate from the fragmentation of an unidentified carbonaceous compound. It is worth noting that a similar increase has not been found for mass number 24, ruling out the presence of appreciable amounts of C_2 radicals as the cause of the mass 12 signal.

The amount of CO production was thought to be significant. With a 1:1 ratio of acetylene to oxygen atom concentration, about 1.5 times as much CO was produced as acetylene, but with acetylene in excess, the amount of CO production was found to equal that of acetylene consumption under any of the investigated conditions. No information on the amount of CO developed could be obtained when N_2 was the major constituent present, because of the overwhelming contribution of N_2 to the signal at mass 28.

The present experiments confirmed our previous finding that in all cases studied the consumption of acetylene is much less than that corresponding to a bimolecular rate law, even under conditions presumably disfavoring the rapid occurrence of secondary reactions involving oxygen atoms, namely, when excess acetylene and low reactant concentrations were employed. This could be explained in either of two ways: (a) the reaction is not truly bimolecular, or (b) the oxygen atom consumption is faster than that of acetylene owing to subsequent reactions. In a subsequent section it will be shown that case (b) is applicable and that between 1.2 and 2.5 times more oxygen atoms are consumed in the overall reaction. The observation of bimolecular kinetics combined with the finding that with excess acetylene the amount of CO production equals that of acetylene consumption suggests the reaction

$$O + C_2H_2 \rightarrow CO + CH_2 - 53 \text{ kcal}$$

Here, keten is the probably intermediate. The possibility of keten formation due to the attachment of oxygen atoms has been demonstrated by Haller and Pimentel (13) using the matrix isolation method of a temperature of 20°K. From photolysis work, energy rich keten is known to decompose yielding CO and methylene, so that the pathway of product formation in reaction (1) can be qualitatively understood.

The present data contained no evidence for the production of CH_2 radicals. This could be explained, (a) by a very rapid subsequent reaction involving CH_2 radicals, which would keep the CH_2 concentration below the limit of detection by means of a signal on mass number 14; and/or (b) by a breakup of CH_2 in the ion source due to dissociative ionization. The lack of information concerning the CH_2 radical is disappointing since one would like to track the further course of the reaction.

Reaction (1) which was first proposed by Fenimore and Jones (14) is at variance with the hydrogen abstraction reaction suggested by Bradley and Kistiakowsky (15) in a mechanism to explain results from shock tube experiments. Hydrogen abstraction could not occur at the low temperatures prevailing in the present experiments because of the involved endothermicity of some ten kilocalories, but it could conceivably play a role at the high temperatures existing in the wake of a shock front. However, the already high value for the rate constant obtained for reaction (1) to be discussed in a subsequent section demands consideration of reaction (1) also at the higher temperatures prevailing in flames, flash photolights and shock tube experiments.

The further course of the reaction can at present only be surmised. Because of the excess consumption of oxygen atoms over that of acetylene, even at high acetylene concentrations, it is clear that reaction (1) is followed by a reaction involving oxygen atoms and methylene radicals. In order to account for the signals observed on mass numbers 12 and 18 it is suggested that

$$(2) \quad O + CH_2 \rightarrow C + H_2O \; -$$

is one of the occurring secondary reactions, although it must be realized that due to the great variety of energetically possible products several pathways exist for the breakup of the intermediate formed from atomic oxygen and methylene. For example, the reaction

$$(3) \quad O + CH_2 \rightarrow CH + OH$$

although 7 kcal endothermic, could nevertheless occur if some of the energy liberated in reaction (1) is contained in the CH_2 radical.

2.3.2 Ethylene. The reaction of oxygen atoms has been investigated using discharged O_2 as the source of oxygen atoms. This study was qualitative, its main purpose to explore the reaction products. In contrast to the results obtained with acetylene a number of radicals could be identified as products. In addition to the products CO and H_2, which were manifest by increases of the peaks at mass numbers 28 and 2, signals were observed at mass numbers 15, 29, 30 and 44, which are interpreted to originate from CH_3, CHO, CH_2O and the (C_2H_4O) complex, in accordance with the views derived by Cvetanovic,(3) from studies under somewhat different conditions. The observation of radicals such as CH_3 and CHO indicates that the apparatus is functioning properly as a radical detector, showing that the lack of products experienced with the oxygen atom-acetylene reaction is real.

Figure 11 shows the results obtained in a series of runs in which the total pressure — due predominantly to O_2 — was 280 microns and

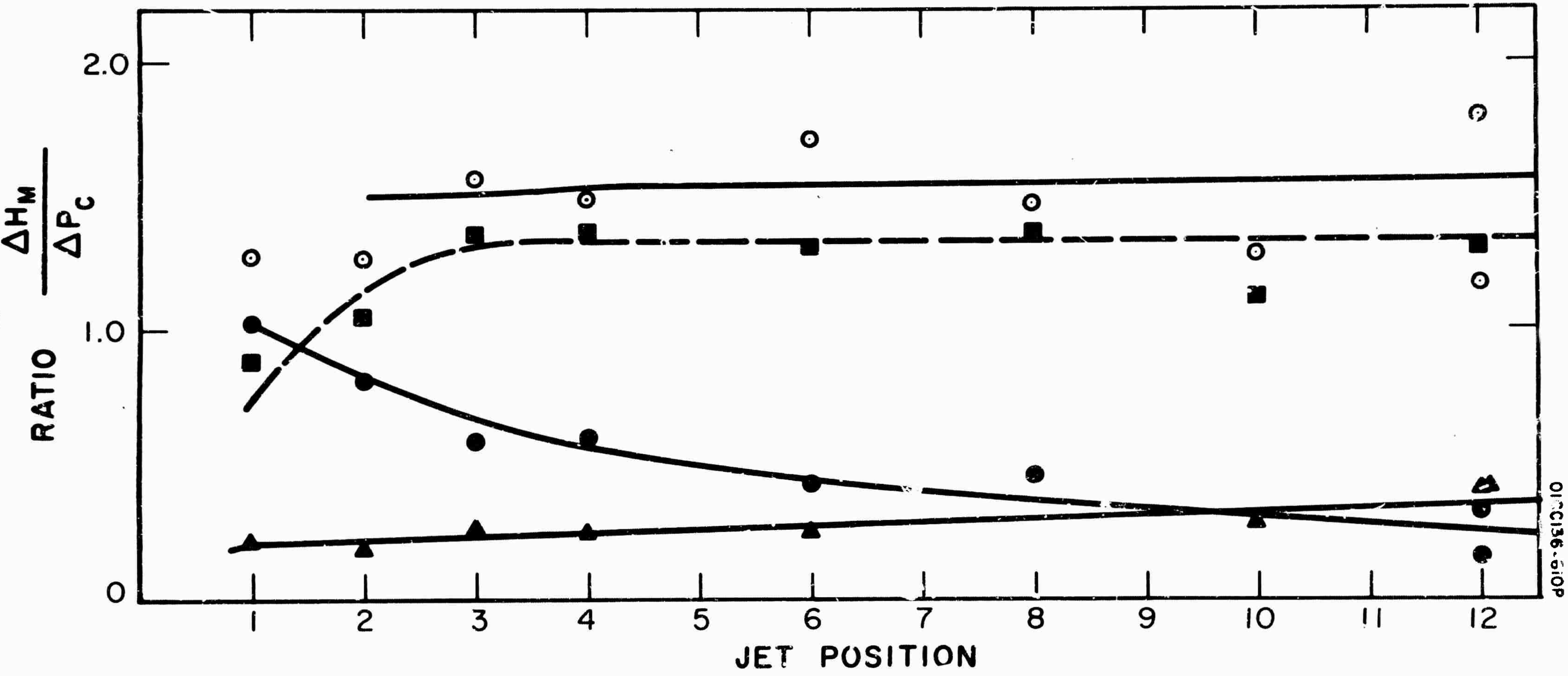


Figure 11. Variation of $\Delta H/P_C$ with variation of jet position: for Mass numbers 15(△); 29 (⊙); 30 (■); 44 (●).

the initial oxygen atom concentration 16.5 microns. Since the initial partial pressure of ethylene underwent a decrease from 21 to 15 microns during the experiments, owing to a depletion of ethylene in the storage bulb, the results are presented with respect to ethylene consumption utilizing the ratio H/P_C, where H is the increase in peak height observed for a product and P_C is the pressure of ethylene consumed.

Little dependence on position (i.e., reaction time) is observed for the peaks at mass 15 and 29, indicating that the corresponding products CH_3 and CHO are probably evolved in the initiation reaction. The ratio for the peak at mass 30 shows a definite time lag, while that for the peak at mass number 44 decreases with time indicating that it belongs to an intermediate. In accordance with the ideas developed by Cvetanovic,(16) the results can be interpreted by the following simple mechanism

$$O + C_2H_4 \rightarrow (C_2H_4O)^* \rightarrow CH_3 + CHO$$

$$O + CH_3 \rightarrow CH_2O + H$$

$$H + CHO \rightarrow H_2 + CO$$

No determination of the rate constants involved were performed but the over-all rate constant for the reaction of oxygen atoms with ethylene is known.

2.3.3 Carbonyl Sulfide. The reaction of oxygen atoms with carbonyl sulfide has been briefly studied, mainly to check the capability of the mass spectrometer as a radical detector, and to investigate the possibility of using COS as a titrant for oxygen atoms. The results were given in detail in the semi-annual report dated 20 July 1964. The dominant reaction mechanism was found to be

$$O + COS \rightarrow SO + CO$$

$$SO + SO \rightarrow SO_2 + S$$

with the rate constant associated with reaction $k = 0.91 \pm 0.14 \times 10^{-14}$ cc/molec. sec. and that for reaction estimated as 4.3×10^{-12} cc/molec. sec. The results will be published in the "Berchite der Bunsengesellschaft" in the near future, as a result of a presentation to this society at its April meeting in Berlin.

<u>2.3.4 Rate Constant for the Reaction of Oxygen Atoms with Acetylene</u>. A major effort has been made in performing a quantitative study of the oxygen atom — acetylene reaction. The basic procedure underlying the experiments is to measure the decay of the oxygen atom concentration simultaneously with the consumption of acetylene. If acetylene is attacked only by atomic oxygen, its concentration can be derived from the integrated rate expression

$$2.3\ \ell g (C_2H_2)_o / (C_2H_2) = k \int_o^t (O) dt$$

regardless of the rate law which is applicable to the removal of oxygen atoms. Accordingly, one can determine the rate constant k from a measurement of (C_2H_2) and $(C_2H_2)_o$, and from the oxygen atom concentration integrated with respect to time. The major difficulty in performing such measurements lies in the accurate determination of the oxygen atom concentration. In the present experiments this was accomplished by monitoring the O-atom concentration on mass 16, using (a) a helium-oxygen mixture to decrease the contribution of molecular oxygen to the mass 16 signal, or (b) producing O-atoms from nitrogen atoms by virtue of the fast reaction $N + NO \rightarrow N_2 + O$. Both methods yielded essentially similar results.

As an example for the type of data obtained, the variation of reactant and product concentration with inlet jet position is shown in Figure 12 for a series of runs in which the linear flow rate of the gas in the reactor was 2430 cm/sec. The initial O-atom concentration was 4.4 microns and that of acetylene 28 microns. It is apparent from the figure that even with large excess concentration of acetylene the consumption of oxygen atoms is about 1.6 times larger than that of acetylene, indicating that oxygen atoms are consumed in a very rapid subsequent reaction. Table 4 shows, for the same series of runs, the data used in the derivation of the rate constant. The lack of trends in the numerical values obtained for the rate constants is taken as evidence that the reaction between oxygen atoms and acetylene proceeds as a bimolecular reaction, providing justification for the applied procedure. Similar data were obtained also under other experimental conditions. In Table 5 are shown the averaged resulting rate constants for 11 series of runs together with the employed parameters. Although these k values exhibit

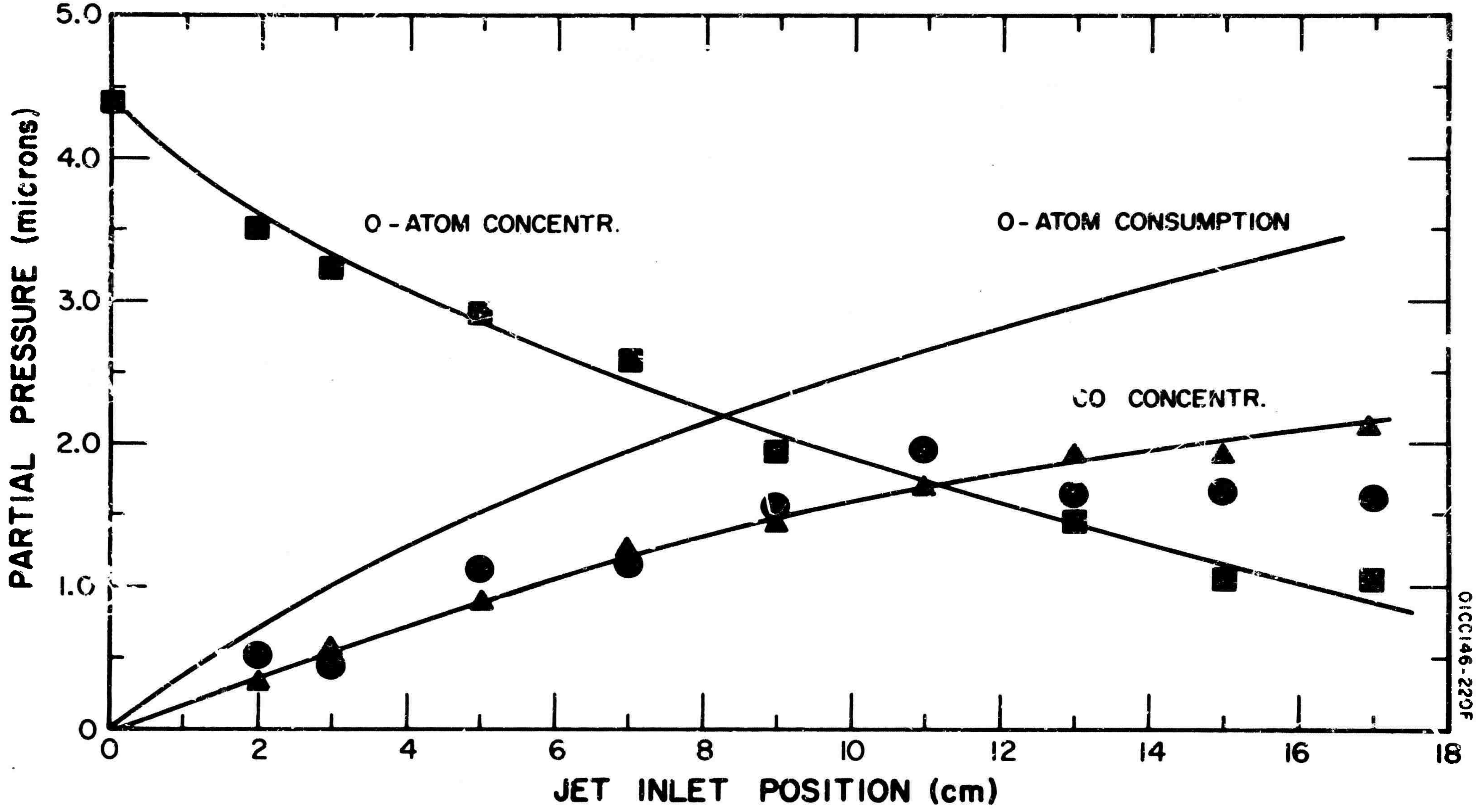


Figure 12. Concentration – time dependence in the Reaction of Oxygen Atoms with Acetylene, ■ – O-atoms; ● – Acetylene ▲ – Carbon monoxide.

TABLE 4

Calculation of rate constant for the atomic oxygen-acetylene reaction using the data shown in Figure 1.

Inlet Position cm	Time millisec	$\int (O)dt$ micron sec.	Δ C_2H_2 microns	$\frac{(C_2H_2)_o}{(C_2H_2)}$	k x 10^{13} cc/molec. sec.
2	0.85	3.42	0.50	1.0182	1.596
3	1.28	4.80	0.50	1.0182	1.138
5	2.12	7.58	1.15	1.0428	1.64
7	2.99	9.81	1.23	1.0459	1.385
9	3.85	11.70	1.[illegible]	1.0558	1.40
11	4.70	13.26	1.98	1.0761	1.660
13	5.56	14.60	1.56	1.0590	1.190
15	6.41	15.70	1.68	1.0642	1.210
17	7.27	16.65	1.68	1.0642	1.134

average k = 1.37 ± 0.22 x 10^{-13}

TABLE 5

Rate Constant for Reaction O + C_2H_2

Partial Pressure (Microns)					k (cc/molec.sec.)
$(O)_o$	$(C_2H_2)_o$	(He)	(O_2)	(N_2)	x 10^{13}
3.3	42.2	544	15	-	1.13
4.5	28	462	13.5	-	1.29
4.4	4.56	435	13.0	-	1.79
4.4	28	435	13.0	-	1.37
4.6	17.4	-	-	500	1.85
2.3	6.[illegible]	-	-	270	1.88
6.0	8.1	-	-	530	1.83
2.6	31	-	-	245	1.24
3.5	1.68	-	-	215	1.22
11	29	-	-	940	1.83
10.8	5.62	-	-	765	1.35

average k = 1.52 ± 0.3 x 10^{-13}

a larger spread than expected from the evaluation of a single series of runs, again no significant trends are noticeable. Thus, the reaction of oxygen atoms with acetylene appears to occur in the same manner regardless of the employed experimental condition. The associated rate constant is . $1.52 \pm 0.3 \times 10^{-13}$ cc/molec. sec. This value is by about an order of magnitude smaller than that known for the reaction of oxygen atoms with ethylene.

2.3.5 Time Dependence of Oxygen Atom Concentration in the Reaction of Atomic Oxygen with Acetylene.

In the analysis of data presented above it has been found that the time dependence of oxygen atom concentration follows an exponential law of the type

$$(O) = (O)_o \exp(-k(C_2H_2)_o \, f t)$$

where f is a factor depending on the ratio $(C_2H_2)_o/(O)_o$. This factor is about 1.2 when $(C_2H_2)_o/(O)_o = 10$ and increases to about $f = 2.5$ for a 1:1 ratio of acetylene to atomic oxygen. Further data analysis is necessary to interpret this finding in the light of the reaction mechanism.

SECTION 3

CONCLUSIONS

Much of the discussion and conclusions have already been given throughout this report. However, it seems worthwhile to emphasize a few points concerning the data obtained for the reaction of O-atoms with acetylene and ethylene.

First one must state that it is impossible at this stage to suggest a complete mechanism for the reaction of either acetylene or ethylene with atomic oxygen. These reactions are undoubtedly very complex and more experimentation may be needed to unravel the completed mechanism. On the other hand, much of the now available data have not yet been analyzed in detail. Pending a complete analysis, then, the following conclusions can be made.

(1) It has been established that the principal light emitting processes in the reaction of oxygen atoms with ethylene are different from the ones taking place in the reaction of oxygen atoms with acetylene.

(2) The rate constant for the reaction of O-atoms with acetylene is $k = 1.5 \times 10^{-13}$ cc/molec. sec., while that for the reaction with ethylene had previously been determined as $k = 2 \times 10^{-12}$ cc/molec. sec. Thus, oxygen atoms react with acetylene about ten times slower than with ethylene.

(3) It has been shown beyond doubt that in the case of the O-atom acetylene reaction the OH emission requires the presence of molecular oxygen and that the OH intensity is proportional to the O_2 partial pressure.

(4) Molecular oxygen and nitric oxide act as quenchers of the other emitters, and this is due to a reaction of oxygen with a non-emitting precursor or precursors.

(5) The observation of similar emissions in the O-atom — acetylene reaction and in the excited argon atom — acetylene reaction indicates that the emission is produced mainly from hydrocarbon species which do not contain oxygen. The reaction of oxygen atoms with acetylene thus serves only as a starter reaction.

(6) Ionization phenomena are not involved in producing these emissions, although they are known to occur in side reactions.

(7) The most important reactions leading to missile trail chemiluminescence involve highly unsaturated hydrocarbons.

Carbon monoxide and water, although the principal by-products of the missile trail are not important sources of light emission.

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