SUBMERGED COMBUSTION OF PREMIXED HYDROCARBON-OXYGEN FLAMES IN LIQUID NITROGEN

by

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I. INTRODUCTION

The possibilities of freezing or isolating free radicals or highly reactive chemical species at very low temperatures have been explored by investigators interested in combustion, rocket propulsion, astronomy, etc. Motivations for immobilizing highly reactive species in these fields of endeavor are diverse:

(1) In combustion, one is frequently interested in the study of the mechanisms by which chemical reactions occur. A logical route is to reduce the rate of reaction by lowering the temperature of the reaction environment, and to thereby be able to observe the short-lived transitory species.

(2) In the field of rocket propellants, one desires to produce a flame of highest possible specific enthalpy. Thus one wants maximum energy in a minimum of mass, and one is then naturally led to consider unusual and highly energetic species.

(3) In astronomy, interest is in making a model atmosphere from a frozen mixture of radicals and energetic compounds from which its activity can be simulated in an environment similar to interstellar space where free atoms and radicals have a long life time, because of a much lower pressure and a much lower temperature (estimated to be in the vicinity of 3.5°K).

However, the practical impact of cryochemistry (the field in which chemical reactions are conducted at temperatures below 100°K) lies in the syntheses of useful substances heretofore unknown, and possibly also some current commercial products by more economical routes. A possible technique for the preparation of unusual molecules is by a flame submerged in a quenching fluid at cryogenic temperatures: in this arrangement, the observed products may be formed in the reaction gaseous flame zone itself as well as from the subsequent reactions of these labile species with the molecules of the cold medium.

It shall be the purpose of this study to develop the technique of submerged combustion at cryogenic temperatures. The technique will then be studied using several simple gases, methane, propane, and acetylene, burning with oxygen and the reaction produce mass will be analyzed for evidence of having trapped unusual products.

II. LITERATURE REVIEW

Flames in General

The kinetics and detailed chemistry of a combustion process are revealed by the composition of the gas within the flame reaction zone. There are four types of species present in flame gases: molecules, free radicals, atoms, and ions. Free radicals are molecular fragments (diatomic or polyatomic) which have one or more unpaired electrons, although they are electrically neutral. The unpaired electron renders the gaseous free radicals highly reactive; hence they, in general, cannot be isolated in pure form at ordinary temperature. Some typical free radicals in hydrocarbon combustion processes are CH_3, OH, C_3H_7, CH_2, etc. Many atoms are also free radicals, i.e., they have an unpaired electron, and those commonly found in flames are H, O, N, Br, etc. Ions are any species possessing a net charge. In a flame, typical distribution ratios of concentrations of molecules, radicals and atoms, and ions are, respectively, $1:10^{-2}: 10^{-7}$.[1]

Free radicals play an important role in the chemistry of flames, as they participate in virtually every flame reaction. They are so reactive that special precautions are required for sampling and analysis. A number of new analytical techniques have been developed, and the most prominent methods for dealing with radicals and unstable species are optical spectroscopy, mass spectrometry and electron spin resonance. Broader and more complete reviews of these analytical tools were described by Minkoff.[2,3]

Investigation of Flame Chemistry by Mass Spectrometry

Of the methods proposed for study of reaction intermediates, the mass spectrometric method appears to be the most versatile and reliable analytical instrument because of its high sensitivity, analytical response to all components, and its capability for quantitative determination of all species.

The capabilities of the mass spectrometer were first explored by Eltenton[4] in studies of the reaction intermediates in the thermal decomposition of methane, ethane, and propylene and in low pressure flames. In order to study the various stages of the flame process, Eltenton developed an oscillating diffusion flame technique which brought molecules, radicals, etc. from different parts of the flame into the mass spectrometer. In this way, he was able to deduce the relative importance of various radicals in different regions of the flame. One of the main results was the identification of the HO_2 radical in flames of methane and propane, under conditions which excluded any confusion with the isotopic $^{16}O\ ^{17}O$.

Foner and Hudson[5] used a molecular beam gas sampling method which they modified to minimize the number of collisions of the gas molecules with the walls of the instrument. The gases from the reaction zone passed through the first orifice as a sonic jet and then into the ion source of the mass spectrometer in such a way that destruction of short-lived intermediates on the walls of the ionizing chamber was reduced to a minimum.

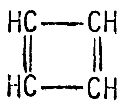
The technique for distinguishing the peaks of radicals from those due to fragments of the parent molecules are also now well established. The qualitative detection of radicals is based on the fact that the ionization potential of a free radical is less than its appearance potential from a given compound by an amount of energy equal to the sum of the strength of the bond broken and the kinetic and internal energies of the fragment formed by electron impact. Such energy differences can be readily measured by controlled energy electron bombardment in the source of the mass spectrometer. The quantitative measurements of radicals have been well discussed by Lossing, Ingold, and Tickner.[6]

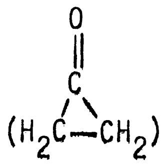
Cryochemistry in General

The discussion thus far has pointed out the feasibility of detection of unstable species not usually found in pure form at ordinary temperatures. Once could extend this branch of research into a new environment in which the completion of the reaction between a radical or an excited species and a second reactant would be retarded by quenching the entire system with a suitable refrigerant. The discussion to follow is not on the trapping and identification of radicals, which has an extensive leterature, but rather on the investigation of highly reactive intermediates (formed from a cryogenic quench reaction) that are not observed at ordinary temperatures, in other words, one is interested in low temperature synthesis. Three benefits can be derived from low temperature synthesis: (1) the elucidation of the mechanism and structure of the unstable intermediates by stopping the reaction before its completion, (2) the direct synthesis of some current commercial chemicals, and (3) the strong possible practical utilization of the new or unusual compounds that may also be obtained. These useful aspects of cryochemistry will now be briefly discussed.

The elucidation of reaction mechanism was well illustrated from the reaction between oxygen atoms and ethane at or above room temperature to give CO, CO_2, CH_3CH_2OH, CH_2O, CH_3CHO and H_2O.[7] However, when the reaction was suddenly quenched at liquid air temperature, only ethanol, C_2H_5OH, was produced. Ethanol was evidently the first species formed before the reaction reached completion.

Other than arresting known and common materials from processes in which that substance may appear as an intermediate, unusual and heretofore unknown compounds may also be produced. For example,[8]

(1) The pyrolysis of cyclobutadiene irontricarbonyl at 380°C and 0.1 torr followed by a cryo-quench to -196°C leads to the production of cyclobutadiene,  .

(2) The smooth reaction between diazomethane and ketene at -150°C yields cyclopropanone  without the use of an

active reagent produced by photolysis, discharge, or other such means.

Another important facet of low temperature synthesis is the potential utilization of new compounds such as oxygen fluoride and the lower boranes. Oxygen fluoride, O_3F_2, an unusual low temperature substance, was the object of much Air Force and NASA study as a potential powerful oxidizer. It was usually made by a discharge in the mixed gaseous elements of O_2 and F_2 at 10 to 25 torr contained in a discharge reactor whose walls were cooled to 65° to 90°K.[9]. O_3F_2, a blood-red liquid at liquid oxygen temperature (90°K), is an extremely potent oxidizer, and when dissolved in liquid oxygen to the limits of its solubility (<1 per cent), O_3F_2 renders the oxygen hypergolic toward hydrogen and low molecular weight hydrocarbons. Similarly, the lower boranes and a variety of alkylated boranes have also received much attention as possible high energy rocket and aircraft fuels.[10]

Low Temperature Synthesis Techniques

Low temperature products were synthesized by a variety of activation techniques in reactor cooled to cryogenic temperatures. These included gaseous discharge, pyrolysis, photolysis and submerged flame techniques. More comprehensive discussions on this subject have been given by McGee and Martin,[11] and by Minkoff.[12, 13]

Gaseous Discharge. In a gas discharge reactor, the discharge disrupted the gas and produced radicals or excited species which contacted a second reactant at low temperature. Dissociation of the gas molecules was due primarily to collision between electrons and molecules. For example, ozone, O_3, was obtained at low temperature by condensation of the effluent from a discharge in O_2 gas.[14] The majority of modern work has been with discharges. Another route was to premix the reactants and to allow the gas mixture to flow into a discharge tube reactor that was immersed in a cryogenic refrigerant.

Pyrolysis. Useful radicals may be thermally produced by breaking chemical bonds under non-equilibrium conditions. For example, azomethane, an unstable compound, may be pyrolized to give simple radicals:

$$CH_3N{=}NCH_3 \rightarrow N_2 + 2CH_3$$

Radicals containing nitrogen could also be produced by thermal decomposition. The labile species were then permitted to react with a second reactant at cryogenic temperature.

Photolysis. Light of the proper wavelength was used to dissociate certain molecules in a fairly specific way, thus leaving the stronger bonds of the molecules unchanged, and, hence, a simpler system of reactants was obtained. From a thermal design point of view, the photolytic process by-passed the problem associated with the necessary proximity of a source of high energy for radical generation and low energy for cryogenic quenching of the reacion species, since these species were here generated in situ.

Submerged Flames. Flames may be divided into two broad classes: premixed and diffusion. Premixed flames are those which have the reactants premixed before entering the reaction zone. If they are not premixed, the resulting flame is called a diffusion flame since the fuel must mix with the surrounding oxidant or air by diffusion in order to burn. Flames were known to burn submerged in cryogenic refrigerants. The rapid cryogenic quench could yield some intermediate species in the combustion as final products. In addition, the direct contact between active flame species and the cryogenic fluid could lead to the formation of unusual compounds. Only a few studies of submerged diffusion flames have been made; some of these are:

(1) A hydrogen diffusion flame in liquid air[15] to give a snowlike, bluish colored solid which was filtered from the solution. NO (nitric oxide) and other unidentified species were formed by vaporizing this blue solid, and the filtrate contained ozone (O_3).

(2) A hydrogen diffusion flame in liquid oxygen to yield O_3 in the filtrate.[15, 16]

(3) An acetylene diffusion flame[17] in liquid air to yield a solid consisting mostly of carbon with some CO_2, H_2O and HNO_3. The filtrate contained O_3.

(4) A hydrogen sulfide (H_2S) diffusion flame[18] in liquid air to yield a solid containg H_2S, SO_2 and H_2O. O_3 and H_2S were found in the filtrate.

Other types of submerged combustion not involving a premixed flame were solids in refrigerants such as sulfur in liquid air, charcoal in liquid air, wood in liquid air,[19, 20] and carbon in liquid O_2.[21]

Another technique to study the intermediates of a diffusion flame was discussed by Stadnik[22] and McKinley.[23] The apparatus was arranged such that the flame burned inside a wetted-wall column. In this way, reactive products of a H_2-O_2 diffusion flame were absorbed in a film of water flowing close to the flame.

Submerged combustion is also used in industry for heating,[24] agitation and evaporation.[25, 26] However, industrial submerged combustion did not involve the direct contact between the flame itself and the liquid. The burner fires into a combustion chamber which extended into the liquid, with exhaust ports located well below the liquid level. Hot products of combustion are thereby forced through the exhaust ports and bubbled up through the liquid. In this way, more heat can be absorbed than in more conventional arrangements.

III. EXPERIMENTAL

Plan of Investigation

Although the submerged flame is an old concept for the preparation of unusual compounds, it has not been studied by modern analytical tools to allow a more exact and detailed investigation. Therefore, the concept of flames quenched in a cryogenic fluid is being revived in this work with the following goals:

(1) To design a system in which a flame reaction could be carried out submerged in liquid nitrogen. The objective is to detect any partially oxidized compounds and, certainly, also any unusual products which might be produced from such a system.

(2) To discover the defects and range of application rather than to solve any particular problem. The outcome of the results would be useful in further system improvements so that future research could be made more effective and precise.

The specific systems to be studied will be the premixed flame of oxygen with hydrocarbon fuels, namely, methane, propane and acetylene in liquid nitrogen.

The Reactor and Related Equipment

The Reactor

An experimental reactor was designed to fulfill two main requirements: (1) To operate a stable premixed flame of hydrocarbon (methane, propane, and acetylene were used) and oxygen beneath the surface of liquid nitrogen, and (2) to allow for mass spectrometric identification of the quenched species from the reactor that were stable at room temperature.

The material of construction was brass because it is easily machined and soldered. All joints were hard-soldered for maximum strength at low temperature. Stainless steel has a lower thermal conductivity (~0.075 watt cm^{-1} deg^{-1} at 77°K) than brass (~0.135 watt cm^{-1} deg^{-1} at 77°K)[27], and it is frequently used in the fabrication of low temperature apparatus, even though it is more difficult to join. Nevertheless only brass was used in the present device.

Schematic diagrams of the reactor are shown in Figures 1 to 3. The three-necked cyclindrical reactor with a side observation port was made from a section of 4-inch O.D. tubing of 1/16-inch wall thickness, and it was 5 1/8 inches in height. The three entry ports and the side observation port were Pyrex glass attached to the reactor with standard Kovar glass-to-metal seals. Port "A", made of 1/2-inch O.D. Pyrex tubing, was about 1/8-inch above the reactor bottom. It served three purposes: (1) to introduce helium gas to flush any unburned fuel left inside the reactor at the beginning of each combustion run, (2) to introduce liquid nitrogen into the reactor, and (3) to provide for a Veeco thermocouple gauge sensor, type DV-1M, for pressure measurements when the reactor was under vacuum; the control unit was Veeco model no. DG 2-2T. Port "B", made of 1-inch O.D. Pyrex tubing, was the exhaust line for the nitrogen vapor and combustion gases. It also served as the port for the insertion and removal of the flame ignitor. When vacuum was required inside the reactor, port "B" was fitted with a Pyrex tube fixture which was connected to two Welch Duo Seal vacuum pumps, model 1405, by means of vacuum rubber tubing; this Pyrex tubing has a high vacuum stopcock which controlled the rate of gas removal from the reactor. Port "C" of 1/2-inch O.D. Pyrex tubing provided the inlet for the reaction products into the mass spectrometer.

The walls of the reactor were insulated with fiberglass and styrofoam, the bottom with fiberglass.

The Flame holder

The flame holder "D" (Figure 2) was a welding torch nozzle, type OX-1, which was threaded to mate into a tapped hole in the brass cylinder "E" in such a manner that the nozzle tip was flush with the inner surface of the cylinder. The brass cylinder served as a heat transfer medium to warm the flame holder as will be explained below. This brass cylinder was soldered to the bottom center of the reactor which had a small center hole to provide the inlet port of the flame holder. A dam "F" (Figure 2) about 1/8-inch high and 1/4-inch in diameter surrounded the flame holder port to stabilize the flame by holding the liquid nitrogen and its gas bubbles away from the nozzle port. The reactant gas inlet of the flame holder was connected by a brass tube "G" (Figure 2) to the mixing chamber of the fuel and oxidant. All joints were hard-soldered.

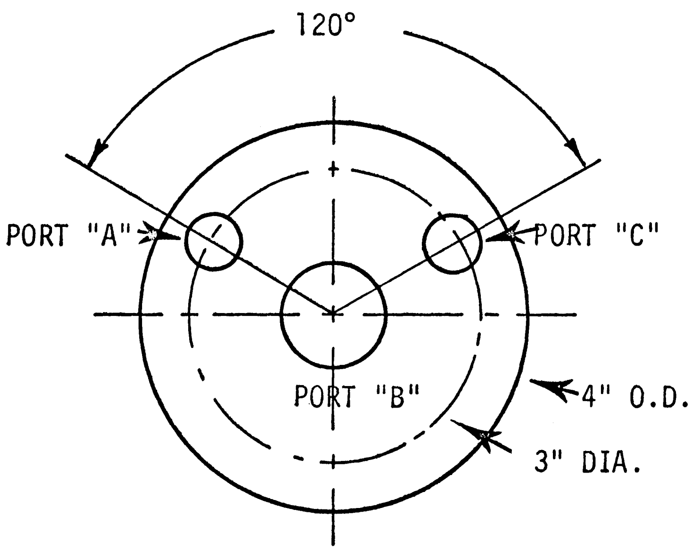


Figure 1 Top View of Reactor Showing the Relative Position of the Entry Ports. Other Details not Shown.

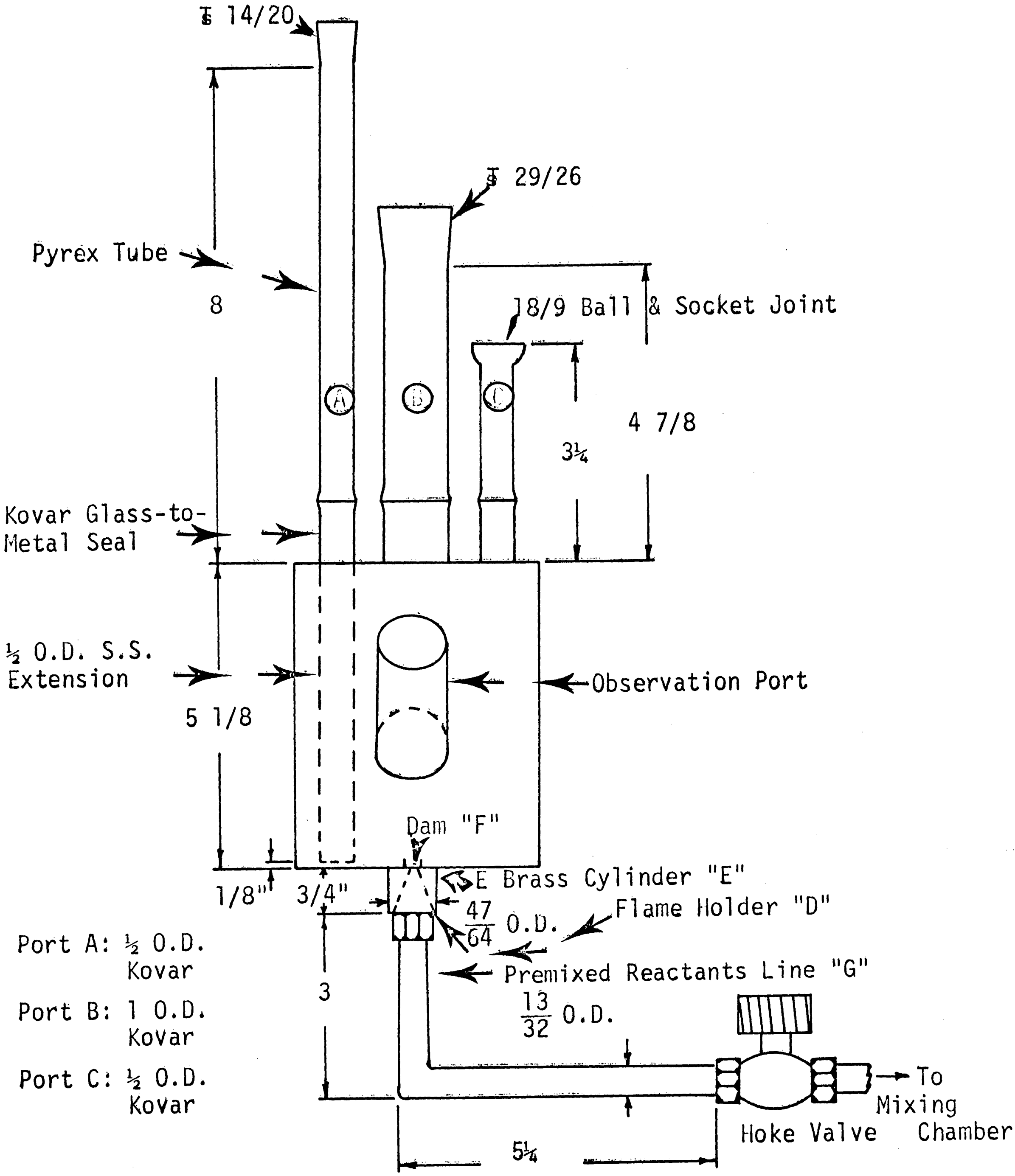


Figure 2 Side View of the Reactor

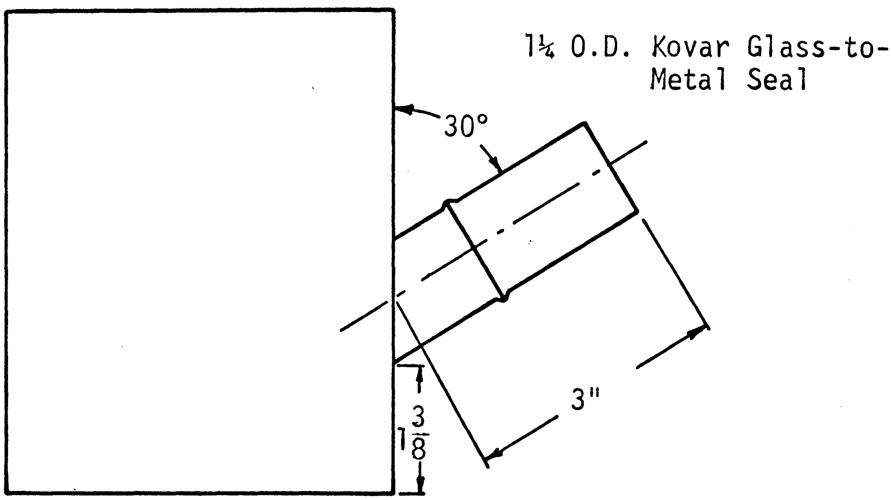


Figure 3 Detail of Side Observation Port

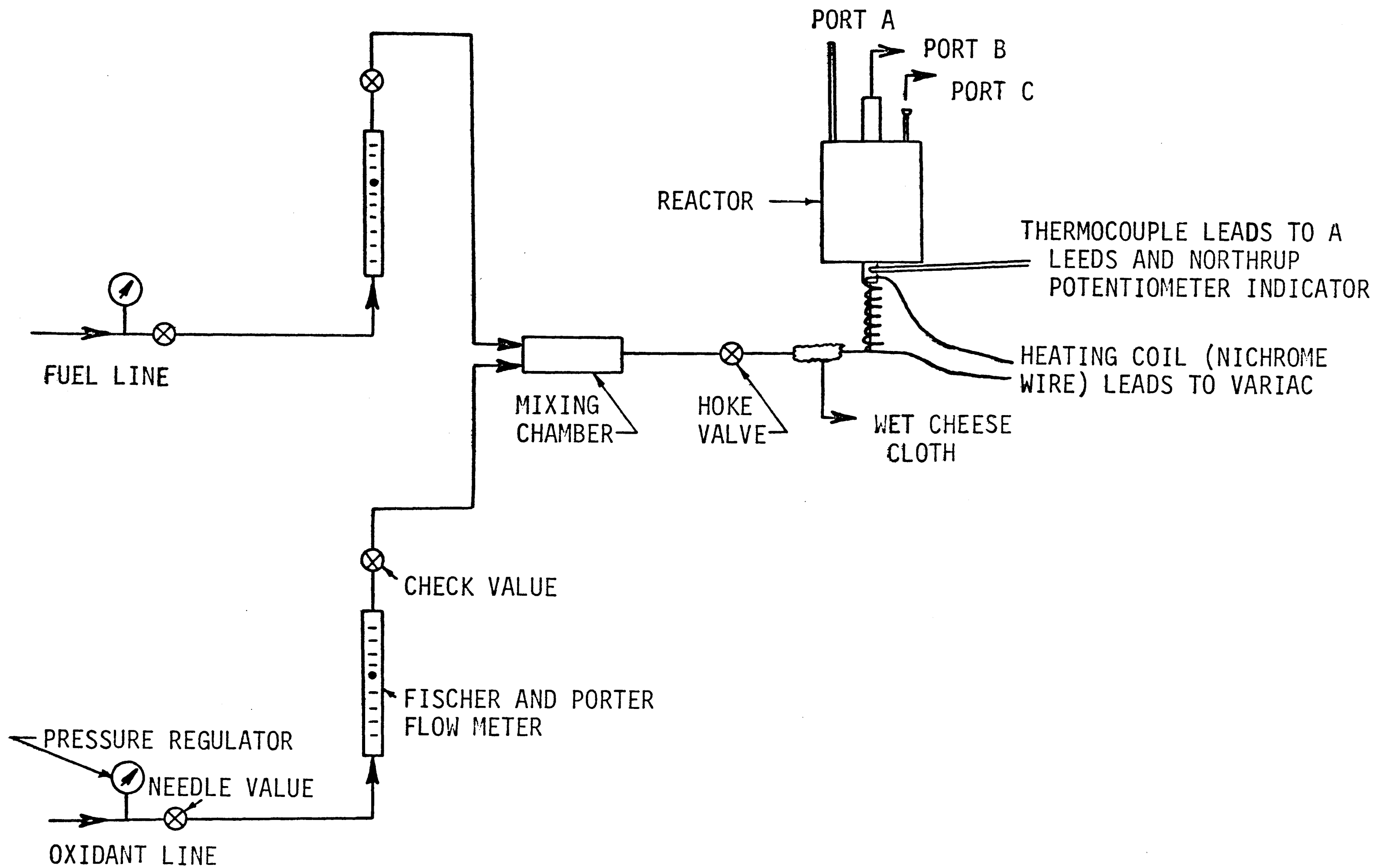


Figure 4. Reactant Flow Arrangement of Cryogenic Submerged Flame System.

The following brief discussion explains the necessity of maintaining a warm nozzle for a self-supporting combustion. Combustion commences with the occurrence of a self-supporting exothermic reaction to produce heat and to highly reactive intermediates, atoms and free radicals. These species participate in chain reactions in each step of which a reactant molecule is consumed and another active species is generated. A stable situation is established when the rate of formation of the reactive species is in equilibrium with the rate of removal. If the flame holder becomes cold, heat loss from the gases to the walls of the flame holder will significantly affect the stability of the flame in that the rate of formation of reactive species is not high enough to maintain a chain reaction. Thus a very cold flame holder will not support a flame.

Since the flame would be quenched by a very cold flame holder when cooled to liquid nitrogen temperature, the nozzle tip was kept at or near room temperature by heating the flame holder by means of a coil of nichrome wire wound around the brass cylinder in which the nozzle itself was mounted (Figure 4). Before winding the heater, the cylinder was electrically insulated with two layers of asbestos paper. To obtain an approximate indication of the temperature, a copper-constantan thermocouple was imbedded at the top section (Figure 4) of the insulated cylinder and was protected by three layers of asbestos paper. Then an eight-foot length of nichrome wire, 1.1 ohms per foot, was wound around the brass cylinder. The cylindrical section was wound twice with two layers of asbestos insulation between the layers of turns of wire. After the winding was complete, the outermost layer of nichrome wire turns was protected by two final layers of asbestos insulation. The two exposed ends of the heating coil were then connected with copper leads to a variac.

The horizontal section of the tube "G" was wrapped with a wet cheese cloth to cool the gas line which would be heated by conduction when the heater of the flame holder was activated (Figure 4). This cooling protected the plastic seat of the Hoke vacuum valve in the gas line from deterioration by the high temperature.

Gas Inlet Systems and the Mixing Chamber

The fuel and oxidant inlet systems to the mixing chamber consisted simply of a pressure regulator, a needle valve, a Fischer and Porter flow meter, and a check valve in each line (Figure 4). The mixing chamber was a National Welding Company hand torch, model no. 3-A Blowpipe. All the gas line connections were made with Tygon tubing. A Hoke bellows seal valve, model A 434, was placed between the mixing chamber and the flame holder to insure a complete shut-off of the premixed gas line when the reactor was under vacuum. This was necessary because the control valves on the torch handle were not of sufficient quality to totally shut off under vacuum.

The F & P Tri-Flat tapered flow meter operated on the principle of the conservation of energy: a restriction placed in the piping system increased the velocity of the fluid stream as it passed the restriction and caused a corresponding pressure reduction. The basic geometries of interest in the meter were float shape and flow area. Tri-Flat meters employed spherical floats, so that the flow area in the meter was the annular cross-sectional space created by the float as it was rising or falling in the tapered tube. Thus basically the meter measured flow by varying the area available for flow.

With a knowledge of the density and viscosity of the measured fluid, the calibration of flow rates of the 1/8-inch meters (model 448-210 for fuel and model 448-211 for oxygen) was done at 84° F (room temperature) and one atmosphere. The detailed calibration procedure was given in the F & P handbook 10A9010.

The following gases were used: (1) methane, 99% min. purity from Airco, (2) propane, 99.5% min. purity from Philips 66, (3) acetylene, 99.6% min. purity from Matheson, and (4) oxygen, 99.6% min. purity from Airco. All the gases were taken directly from the cylinders with no attempt toward further purification.

The Flame Ignitor

Since the flame holder was located at the bottom center of the reactor, the gas mixture was ignited by means of a nichrome wire ignitor positioned above the dam of the flame holder port. The heating coil of the ignitor (Figure 5) consisted of about seven inches of nichrome wire, 1.1 ohms per foot, wound in 5/32-inch diameter turns, and the two ends were connected by means of alligator clips to two long insulated copper leads connected to a variac. The copper leads were held straight by fastening them to a stiff wire to facilitate the introduction and quick removal of the ignitor through port "B". The last six inches of the ignitor, including the alligator clips, were insulated with asbestos paper to prevent the scorching of the ignitor material when the flame was established.

Experimental Procedure

Methane-Oxygen Submerged Flame

Before adding the refrigerant, the premixed fuel and oxidant mixture at the flame holder of the reactor was ignited in the following manner. Oxygen was passed into the reactor for about a minute to flush the reactor. At this point, the flow rate of oxygen was not critical. Afger a minute, the oxygen flow was decreased to a minimum (about 2.1 mmoles/min) that would insure a satisfactory ignition of the premixed gases when the fuel line was opened. The ignitor, positioned about 1/8 inch above the dam of the nozzle, was then turned on. With the ignition coil red hot, the fuel line was opened just enough to start a flame. If the fuel flow is larger than necessary, the ignitor coil will be cooled and ignition will not occur. A caution should be noted here. If ignition does not occur after some ten to fifteen seconds, the gas lines must be closed, and the reactor must be purged with helium gas for a new start. Otherwise an explosion will occur from the fuel-oxidant mixture now filling the reactor when the ignitor is activated.

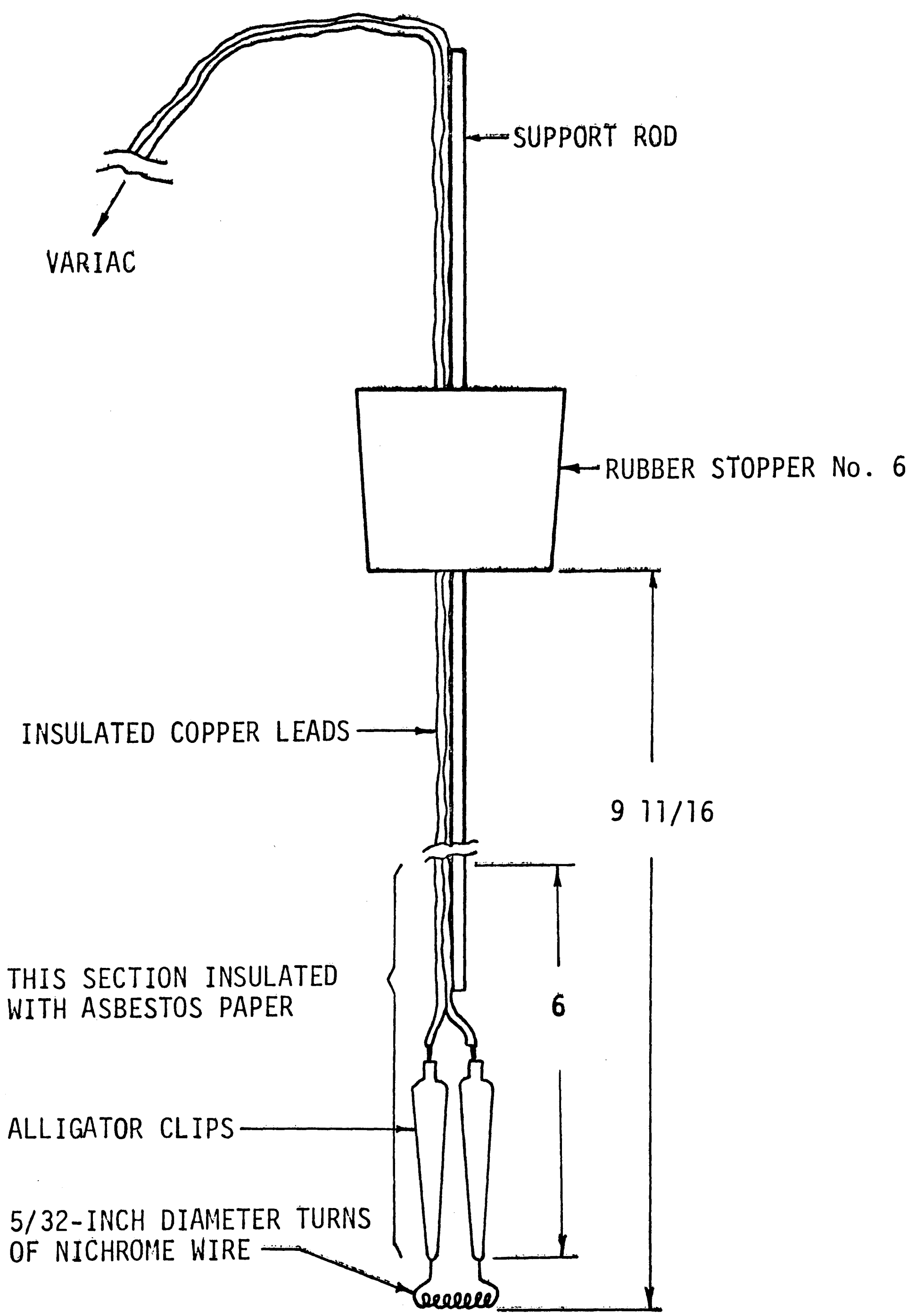


Figure 5. Flame Ignitor. Insulation of Alligator Clips Not Shown.

After the flame was established, the ignitor was quickly removed, and the oxygen and fuel valves were adjusted to the desired flow rates and stoichiometry.

The submerged flame in liquid nitrogen was operated in the following way. First the heating element of the brass cylinder was turned on (variac set at about 30) to increase the temperature of the flame holder, then liquid nitrogen was slowly poured into the reactor through tube "A". Cautious addition was necessary to prevent the flame from being blown out by the initial vigorous boiling of liquid nitrogen from the warm surfaces of the reactor. After this initial vigorous boiling had decreased, liquid nitrogen could be introduced at a faster rate. At the same time, more power was provided to the heating element to maintain a warm flame holder to support the flame. The flame was submerged when the definite long oval shape of the flame in the air became a blurry bluish glow beneath the surface of liquid nitrogen.

Three sets of CH_4-O_2 submerged flame conditions were used and are summarized in Table 1.

The calculated amount of liquid nitrogen required to quench the combustion products to the boiling temperature of liquid nitrogen, 77° K, is shown in sample calculations section that appears in Appendix B. A comparison between the experimental and calculated values for the stoichiometric mixture in Table 1 indicated that heat leaks from the bottom and the walls of the reactor accounted for almost two-third of the actual amount of liquid nitrogen used (experimental rate/calculated rate ~3).

Table 1. Methane-Oxygen Submerged Flame Experimental Conditions

CH_4-O_2 Mixture	O_2 mmoles/min	CH_4 mmoles/min	Liq. N_2 Required, cc/min Experimental	Liq. N_2 Required, cc/min Calculated	Approximate Temp. of Brass Cylinder Surface °C
Stoichiometric	31.9	14.7	300	90	105
10% O_2-rich	34.1	14.7	300	--	135
10% CH_4-rich	31.9	16.1	300	--	135

Propane-Oxygen Submerged Flame

The premixed C_3H_8-O_2 submerged flame experiments were similar to those of the premixed CH_4-O_2 flame. Three sets of combustion conditions were used, and they are summarized in Table 2.

For the stoichiometric mixture in Table 2, the ratio of the experimental value over the calculated value for the liquid nitrogen consumption rate was about 4.5. Thus in this case, heat leaks into the reactor were larger than those of the previous system, most likely caused by heat conduction from a hotter brass cylinder to the bottom of the reactor.

Acetylene-Oxygen Submerged Flame

The ignition of the C_2H_2-O_2 flame was different from that of the previous systems. It was found by trial and error that acetylene alone should be ignited first with air inside of the reactor, then oxygen was adjusted later. When small amounts of oxygen and acetylene were premixed and ignited, the flame blew out with a loud "pop", and black soot was seen in the acetylene Tygon tubing for about two feet. This was probably a backfire resulting from the torch being operated at low pressures.

The procedure for starting the flame was as follows: with the ignitor red hot, the acetylene valve was slightly opened. After the flame was formed, the flow rate of C_2H_2 was increased to 17.4 mmoles/min. At this point, there was a large emission of black soot from the flame. Immediately the oxygen valve was opened to allow enough oxygen to produce a bright yellow flame with no soot. The acetylene

Table 2. Propane-Oxygen Submerged Flame Experimental Conditions

C_3H_8-O_2 Mixture	O_2 mmoles/min.	C_3H_8 mmoles/min.	Liq. N_2 Required, cc/min Experimental	Liq. N_2 Required, cc/min Calculated	Approximate Temp. of Brass Cylinder Surface °C
Stoichiometric	43.9	8.8	600	130	115
15% O_2-rich	50.5	8.8	600	-	125
15% C_3H_8-rich	43.9	10.1	600	-	125

flow rate of 17.4 mmoles/min was the minimum (determined by many trials) which allowed a stable acetylene flame during the oxygen adjustments to the desired experimental conditions. A lower fuel flow rate would make the flame unstable to the changes in the oxygen flow rates. This minimum value was probably determined by the geometry of the nozzle in the partially closed reacotr.

Two sets of submerged combustion conditions were used, and they are summarized in Table 3.

Heat leaks into the reactor accounted for almost half of the actual amount of liquid nitrogen used (experimental rate/calculated rate ~2).

Method of Product Identification

After the flames had burned submerged in liquid nitrogen from five to ten minutes, the combustion was stopped, and preparations were made to establish the required conditions for reaction product analysis in the mass spectrometer.

The general procedure for reaction product identification was as follows:

(1) After five to ten minutes of submerged combustion, the flame was cut off by closing the gas supply valves and the Hoke vacuum valve in the premixed gas line to the flame holder.

(2) The heater on the brass cylinder holding the flame holder was turned off.

(3) Port "C" was connected to a Bendix time-of-flight (TOF) mass spectrometer (model 14-107) inlet by Pyrex tubing.

Table 3. Acetylene-Oxygen Submerged Flame Experimental Conditions

C_2H_2-O_2 Mixture	O_2 mmoles/min	C_2H_2 mmoles/min	Liq. N_2 Required, cc/min Experimental	Liq. N_2 Required, cc/min Calculated	Approximate Temp. of Brass Cylinder Surface* °C
Stoichiometric	43.6	17.4	300	140	135
10% O_2-rich	48.0	17.4	300	-	145

* New heating coil wound on brass cylinder.

(4) The Veeco thermocouple gauge sensor was placed into port "A".

(5) The Pyrex arm leading to the two vacuum pumps was fitted into port "B". This connection could be made before the start of the experiments for the CH_4-O_2 and C_2H_2-O_2 submerged flames because port "B" provided a sufficient exhaust port for the gases under the given experimental conditions. However, for the C_3H_8-O_2 system, both ports "B" and "C" were required due to the larger exhaust rates of nitrogen and combustion product gases. Both pumps were turned on before the Pyrex arm was placed into port "B" to prevent a positive pressure build-up in the closed reactor due to the continuous boiling of the liquid nitrogen.

After the above sequence was accomplished, a sample of vapor from the reactor was admitted to the mass spectrometer by slightly opening the mass spectrometer inlet valve so as not to exceed the mass spectrometer maximum operating pressure of 3×10^{-5} torr. Above this pressure, the instrument was designed to automatically turn itself off as a safety feature. In this way, the product vapors were being continuously monitored before and after the completion of the removal of liquid nitrogen and during the reactor warm-up to room temperature. The mass spectra of the reaction products were visually monitored with a Tektronix oscilloscope, type 543A, and recorded on a Honeywell 906 Visicorder. Each time a mass spectrum was recorded, the time, the approximate inside pressure of the reactor as measured by the Veeco gauge sensor, and the approximate temperature of the brass cylinder were also noted. (The heater of the flame holder was off.) The monitoring was stopped when the cracking pattern, as observed on the oscilloscope, did not show any more significant changes as the reactor came to thermal equilibrium at room temperature.

IV. RESULTS AND DISCUSSION

In the submerged premixed flame experiments, a primary objective was to observe any unusual product formed by the quenching process that was stable enough to be identified at room temperature. The results obtained from each type of submerged flame indicated that no significant change in product formation among the three systems was found. Therefore this section will present a detailed discussion of the results from one system; the similar results from the other two systems will be briefly summarized.

Acetylene-Oxygen Submerged Flame

Acetylene-oxygen submerged premixed flame experiments were carried out under two different experimental conditions to study the effects of varying the stoichiometry. The two conditions were: (1) stoichiometric mixture of reactants, and (2) 10 per cent oxygen-rich mixture.

Stoichiometric Mixture

After the submerged acetylene-oxygen combustion was stopped and the reactor was suitably prepared for product sampling, the mass spectrometer inlet valve was slightly opened to admit the combustion products along with nitrogen vapor from the boiling liquid nitrogen still remaining in the reactor. The product identification was based on the volatility of the compounds and on the known mass cracking patterns given respectively in Tables 6 and 7 of Appendix C. It should be noted that the mass spectral data in Table 7 were measured with a magnetic deflection mass spectrometer and, therefore, would not exactly agree with the relative intensities of mass spectra recorded on the time-of-flight mass spectrometer that was used in this work. Because maximum sensitivity of the mass spectrometer was used to observe small ion peaks, large peaks such as N_2, O_2, and H_2O were off scale. Consequently, relative abundances of the ion peaks were not deduced. The only interesting peak from the spectrum (Figure 6) of the first sample during the warm-up of the reactor was at mass number 44, indicating the possibility of CO_2 and/or N_2O. O_2. N_2 and H_2O were also present. The existence of CO, mass number 28, could not be ascertained in these preliminary experiments because it was masked by a nitrogen peak also at the same mass number. A summary of the possible compounds is listed in Table 4.

The next spectrum, Figure 7, was recorded at a higher temperature with no liquid nitrogen remaining in the reactor. Additional peaks were observed at mass numbers 46, 30, 22 and 12. Table 5 presents a summary of possible compounds giving rise to these peaks. Much CO_2 was present as revealed by strong peaks at mass numbers 44, 22 and 12. The presence of NO, N_2O and NO_2 was suggested by an ion peak at mass number 30. However, the separation of NO and N_2O presented some problems. Due to a lack of control of the rate of temperature warm-up of the condensed products inside the reactor, the time interval between the evolution of NO and N_2O was short, and, therefore, the nitric oxide (NO) peak could be masked by a fragment ion NO^+ from the parent molecule N_2O. Similarly, the detection of N_2O was complicated by the presence of CO_2 because both molecules evolved at about the same time and had a common mass number 44. The presence of NO_2 was indicated by two characteristic peaks at mass numbers 46 and 30. Here, the confirmation of NO_2 was clear because of its distinct mass cracking pattern enhanced by its lower volatility when compared to the relatively close volatility of NO and N_2O.

As the reactor became warmer, more NO_2 and less CO_2 were observed as shown in the mass spectrum of Figure 8. The increase of NO_2 was indicated by a large ion peak at mass number (m/e) 30. At this point, a general correlation could be made between the appearance of carbon oxides and nitrogen oxides, based on spectra of Figures 7 and 8 and other spectra from the other two systems: the abundance of the characteristic peaks of carbon oxides at mass numbers 22 and 12 varied inversely with that of mass numbers 30 and 14 of nitrogen oxides. In addition, NO_2 could be generally distinguished from N_2O by comparing the relative abundance ratios of mass numbers 30 over 14 between the two compounds (30/14 = 10 for NO_2 and 30/14~2.4 for N_2O), assuming the contribution from the background nitrogen peak 14 was known.

Figure 9 shows a spectrum near room temperature. Peaks of O_2, N_2, and H_2O were prominent. An interesting peak at mass number 30 probably originated from HNO_3; this peak will be discussed further below.

The last spectrum taken when the reactor bottom was above room temperature (the heater of the flame holder was turned on) is shown

Sensitivity: 11

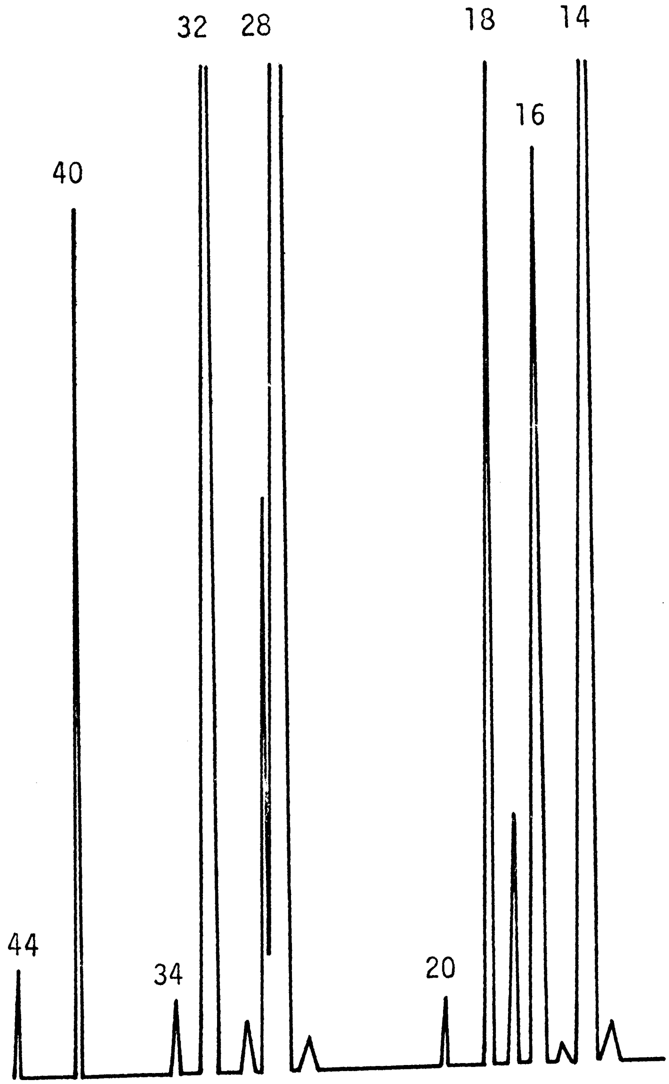


Figure 6 Mass Spectrum of Reaction Products of Stoichiometric C_2H_2-O_2 Flame. Liquid N_2 still Remaining in Reactor.

Table 4. Mass Spectrum of the Reaction Products (Liquid Nitrogen Still in the Reactor) at 70 eV.

m/e*	Possible Compounds
44	CO_2 or N_2O (nitrous oxide)
40 (20d**)	A (argon)
32 (34i***, 16)	O_2
30	Trace
28 (29i, 14)	N_2
27	Trace
18 (17)	H_2O
15	Trace
13	Trace

* The masses in parentheses were fragment ions from the parent ions.

** d = doubly charged ion.

*** i = isotopic ion.

Sensitivity: 7

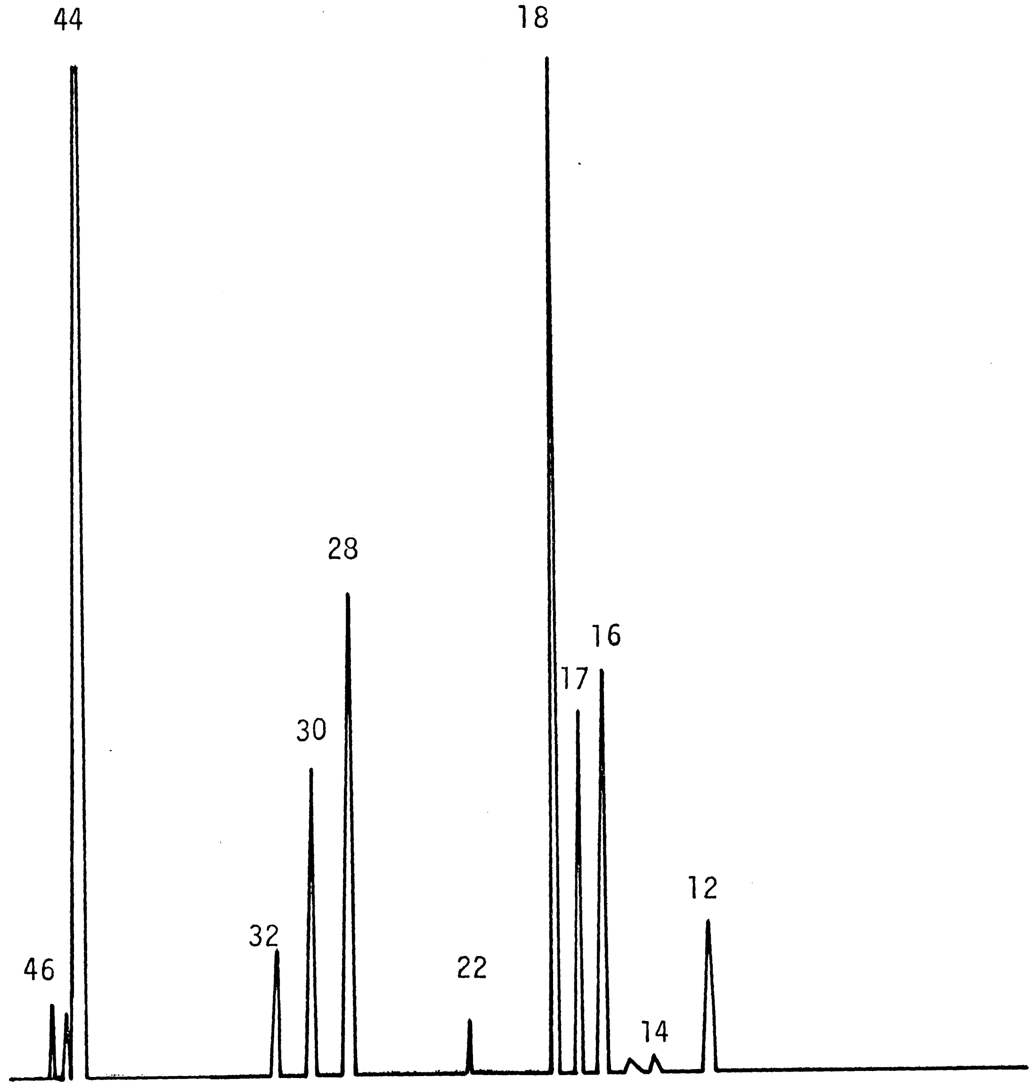


Figure 7 Mass Spectrum of Reaction Products of Stoichiometric C_2H_2-O_2 Flame. No Liquid N_2 in Reactor. Approximate Temp. of Flame Holder: -169°C.

Table 5. Mass Spectrum of the Reaction Products (No Liquid Nitrogen Inside the Reactor) at 70 eV.

m/e	Possible Compounds
46 (30)	NO_2
(45i*, 22d**, 12)	CO_2
44	
(30)	N_2O
32 (16)	O_2
28 (14)	N_2
18 (17)	H_2O

* i = isotopic ions.

** d = doubly charged ions.

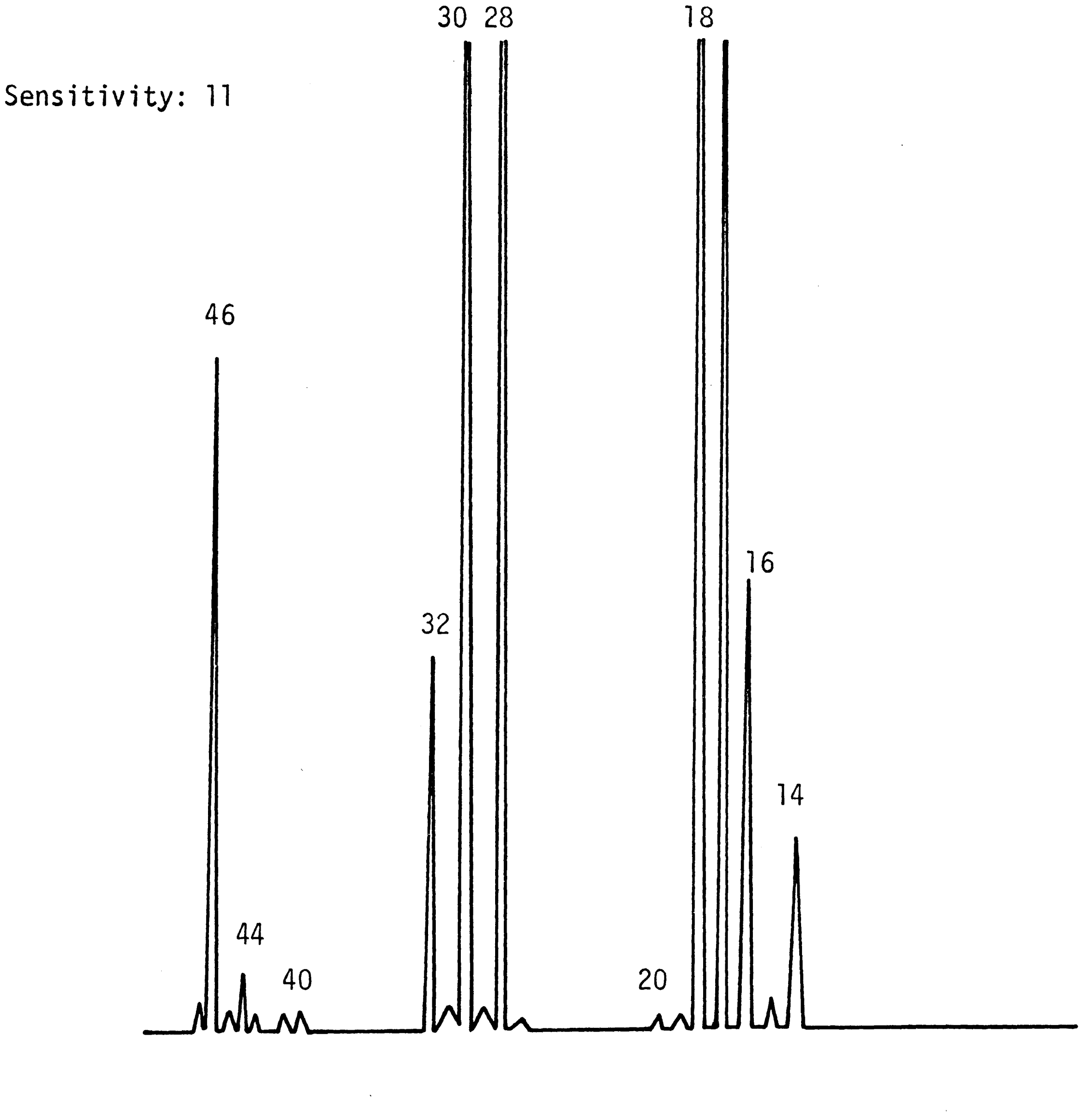


Figure 8 Mass Spectrum of Reaction Products of Stoichiometric C_2H_2-O_2 Flame. No Liquid N_2 in Reactor. Approximate Temp. of Flame Holder: -91°C.

in Figure 10. Three large peaks were observed at mass numbers 46, 44, and 30. Peaks 46 and 30 were assigned to HNO_3. HNO_3 has a higher boiling point than previous compounds observed, and auto-ionizes[28] by the following equation,

$$2\ HNO_3 = NO_2^{+} + NO_3^{-} + H_2O.$$

Thus the presence of HNO_3 was characterized by a mass cracking pattern of NO_2 ion recorded at a temperature above room temperature.

The presence of carbonic acid (H_2CO_3) was suggested by peak 44: carbonic acid decomposes into H_2O and CO_2 on heating.

10 Per Cent Oxygen-Rich Mixture

The premixed flame with 10 per cent excess oxygen apparently did not bring about any additional compounds than those just reported for the case of the stoichiometric premixed flame (Figure 11 to 15). Here one would have expected to obtain some oxygen containing compounds because of the relative abundance of oxygen atoms.

The sequence of evolution of the reaction mass inside the reactor during warm-up under both experimental conditions could be summarized in the order of their decreasing volatility: CO (probable existence), NO (probable existence), N_2O (probable existence), CO_2, NO_2, H_2O, HNO_3 and some H_2CO_3.

Methane-Oxygen and Propane-Oxygen Submerged Flames

Submerged combustion for the methane-oxygen system was carried out at three different experimental conditions: (1) stoichiometric

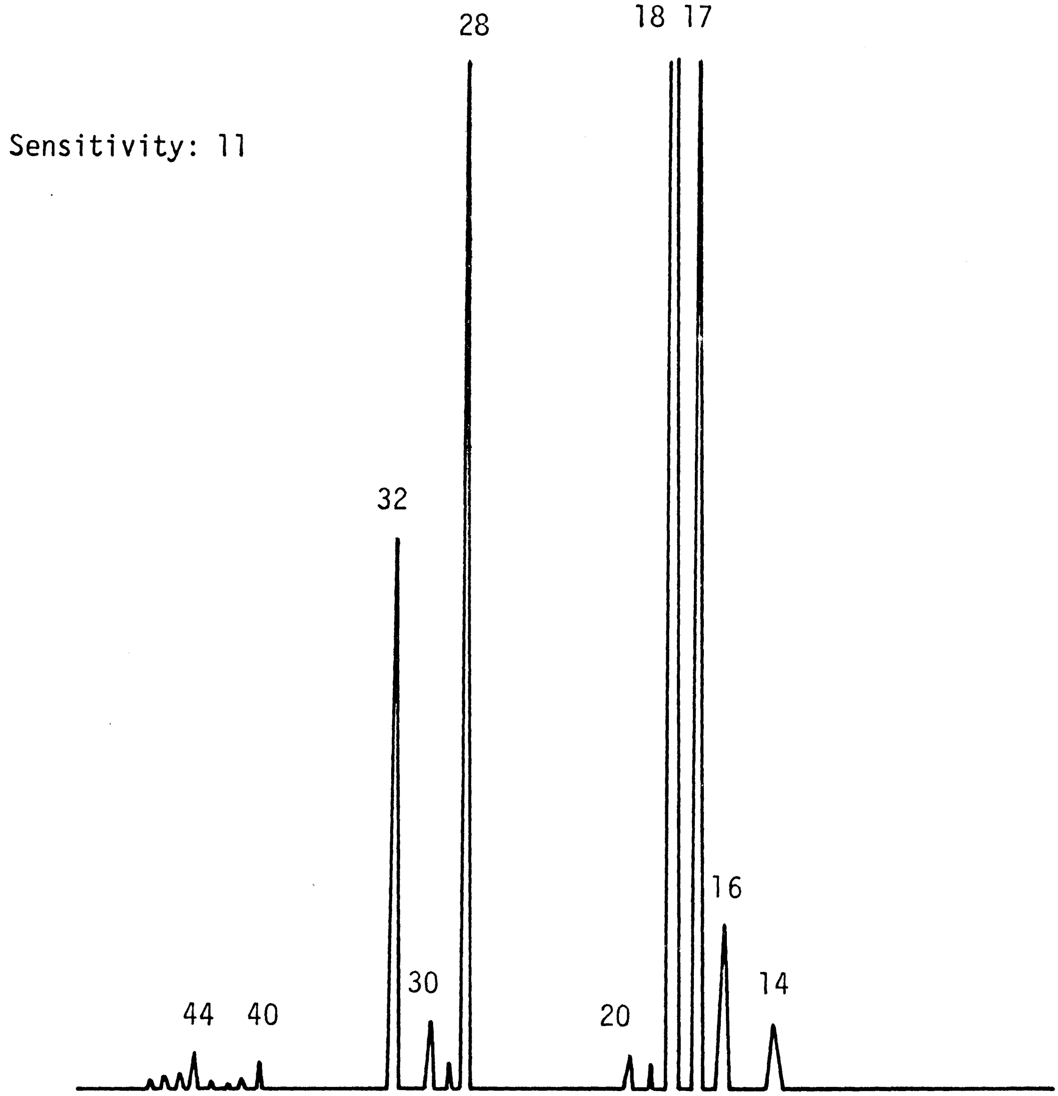


Figure 9 Mass Spectrum of Reaction Products of Stoichiometric C_2H_2-O_2 Flame. No Liquid N_2 in Reactor. Approximate temp. of Flame Holder: 26°C.

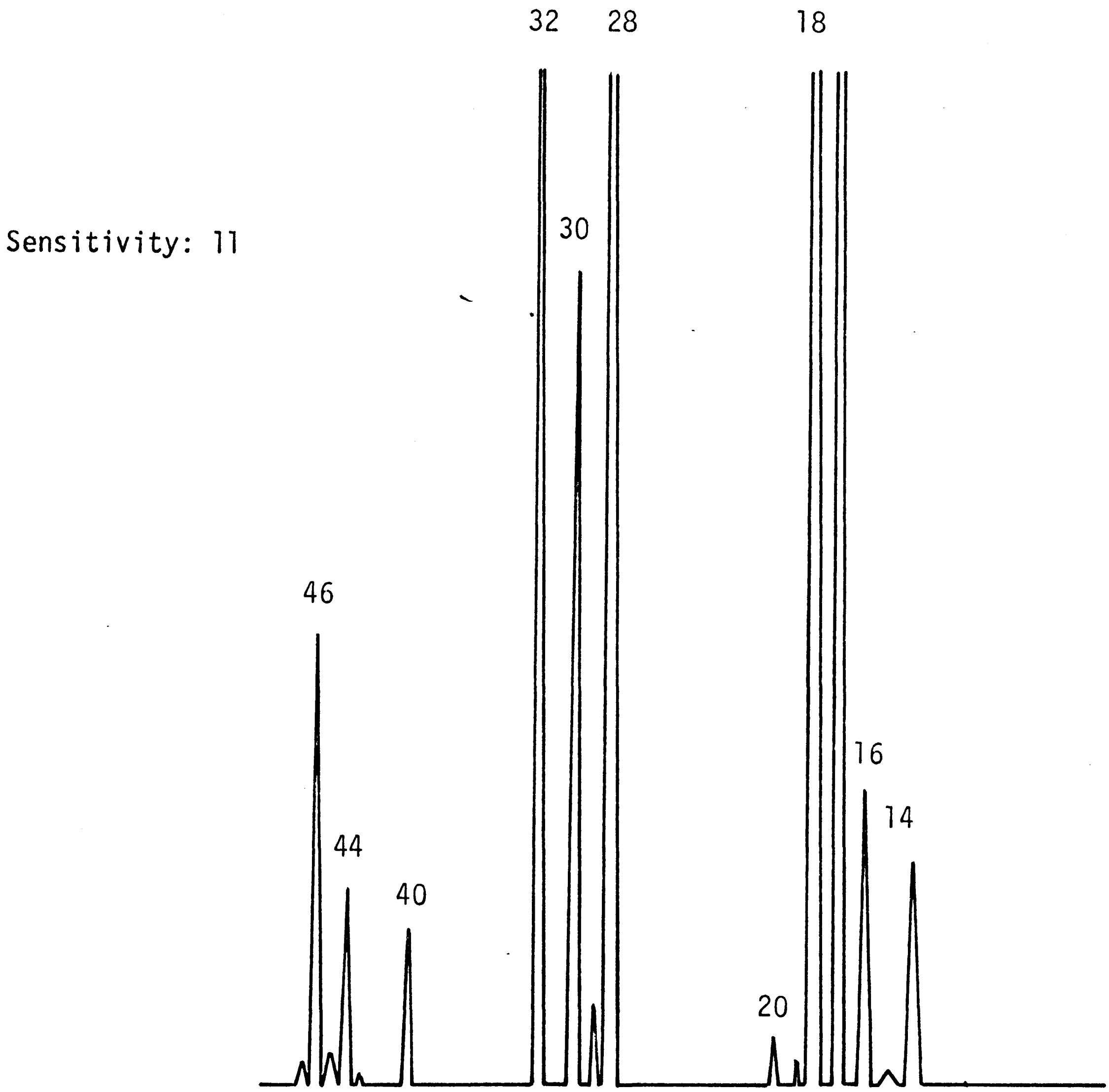


Figure 10 Mass Spectrum of Reaction Products of Stoichiometric C_2H_2-O_2 Flame. No Liquid N_2 in Reactor. Approximate Temp. of Flame Holder: 156°C.

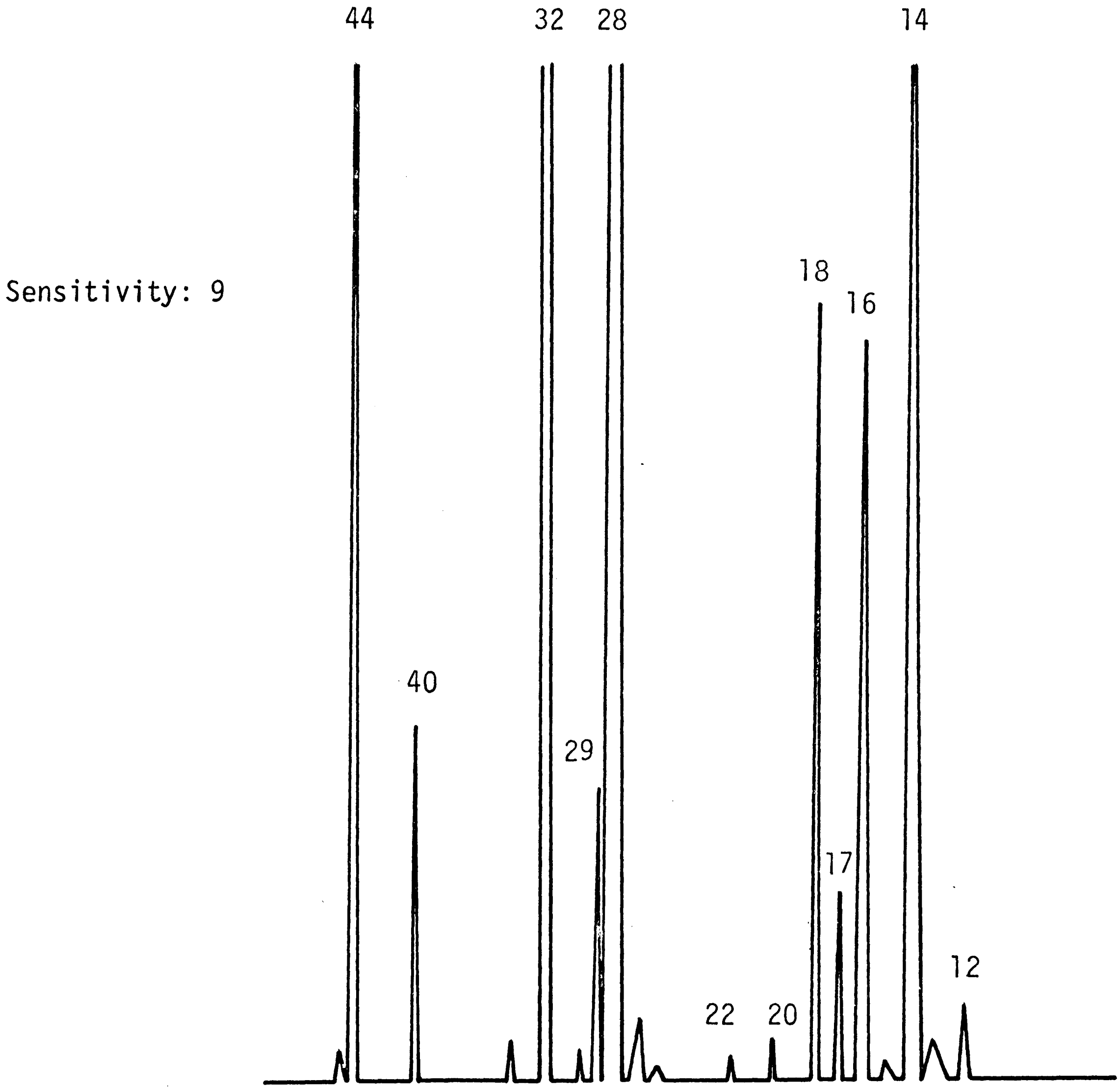


Figure 11 Mass Spectrum of Reaction Products of C_2H_2-O_2 Flame with 10 per cent Excess of O_2. Liquid N_2 still Remaining in Reactor.

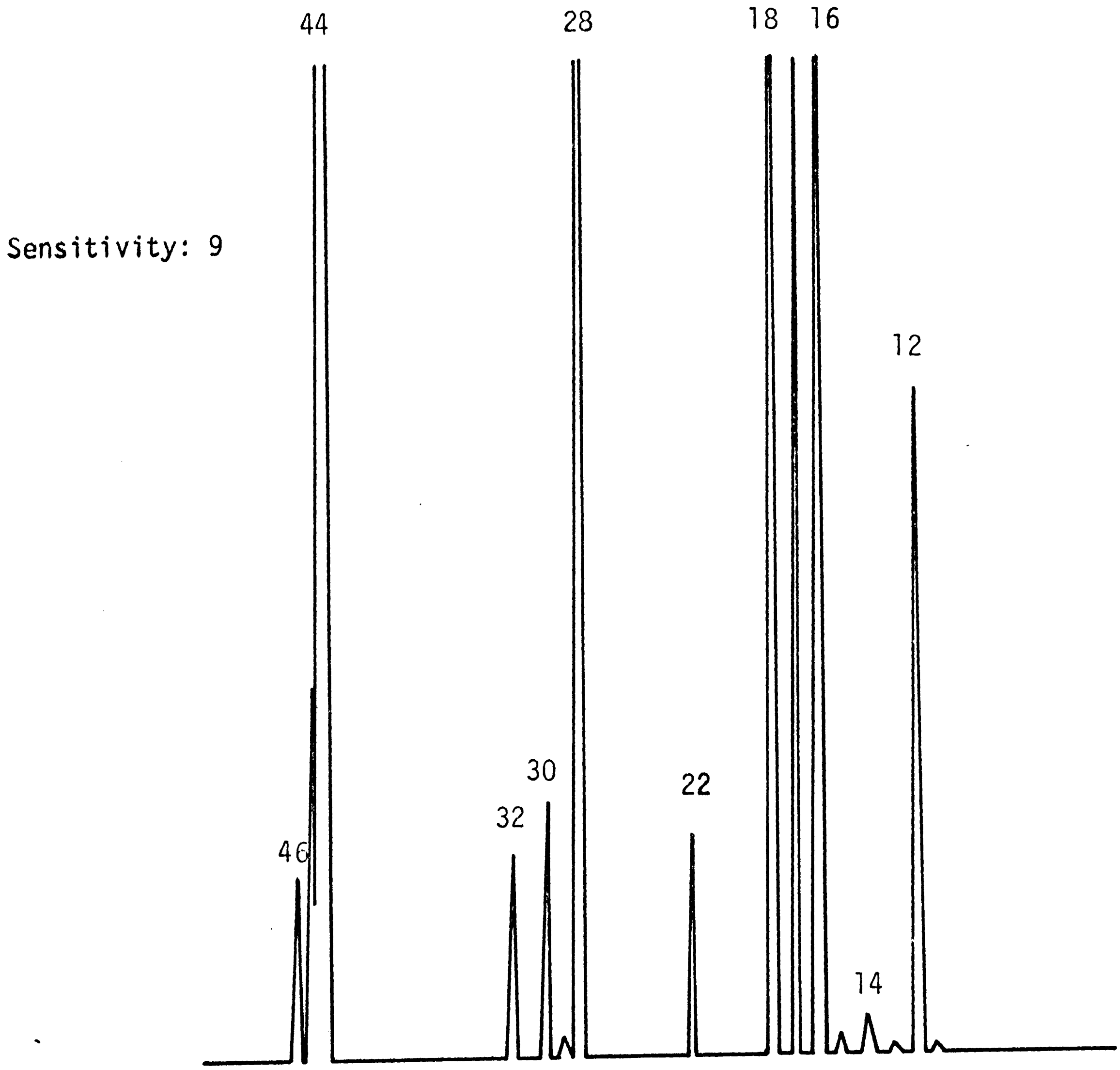
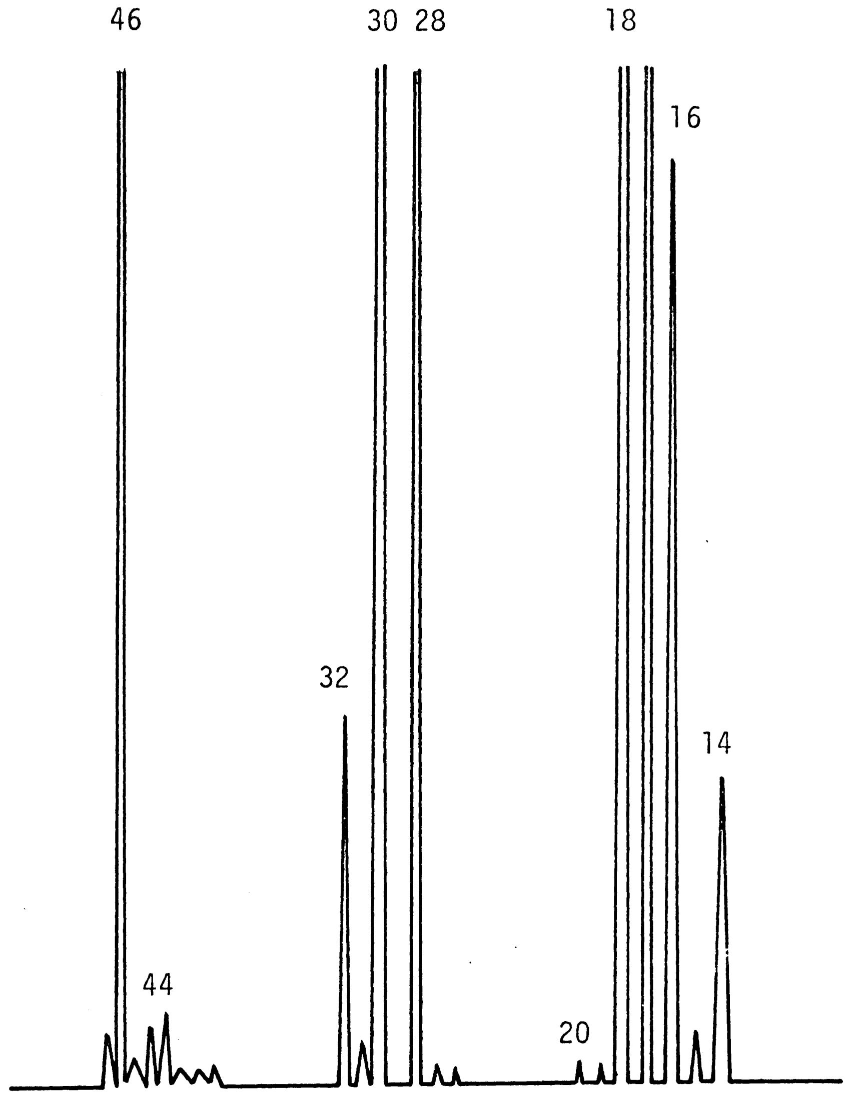


Figure 12 Mass Spectrum of Reaction Products of C_2H_2-O_2 Flame with 10 per cent Excess O_2. No Liquid N_2 in Reactor. Approximate Temp. of Flame Holder: -169°C.



Sensitivity: 11

Figure 13 Mass Spectrum of Reaction Products of C_2H_2-O_2 Flame with 10 per cent Excess O_2. No Liquid N_2 in Reactor. Approximate temp. of Flame Holder: -106°C.

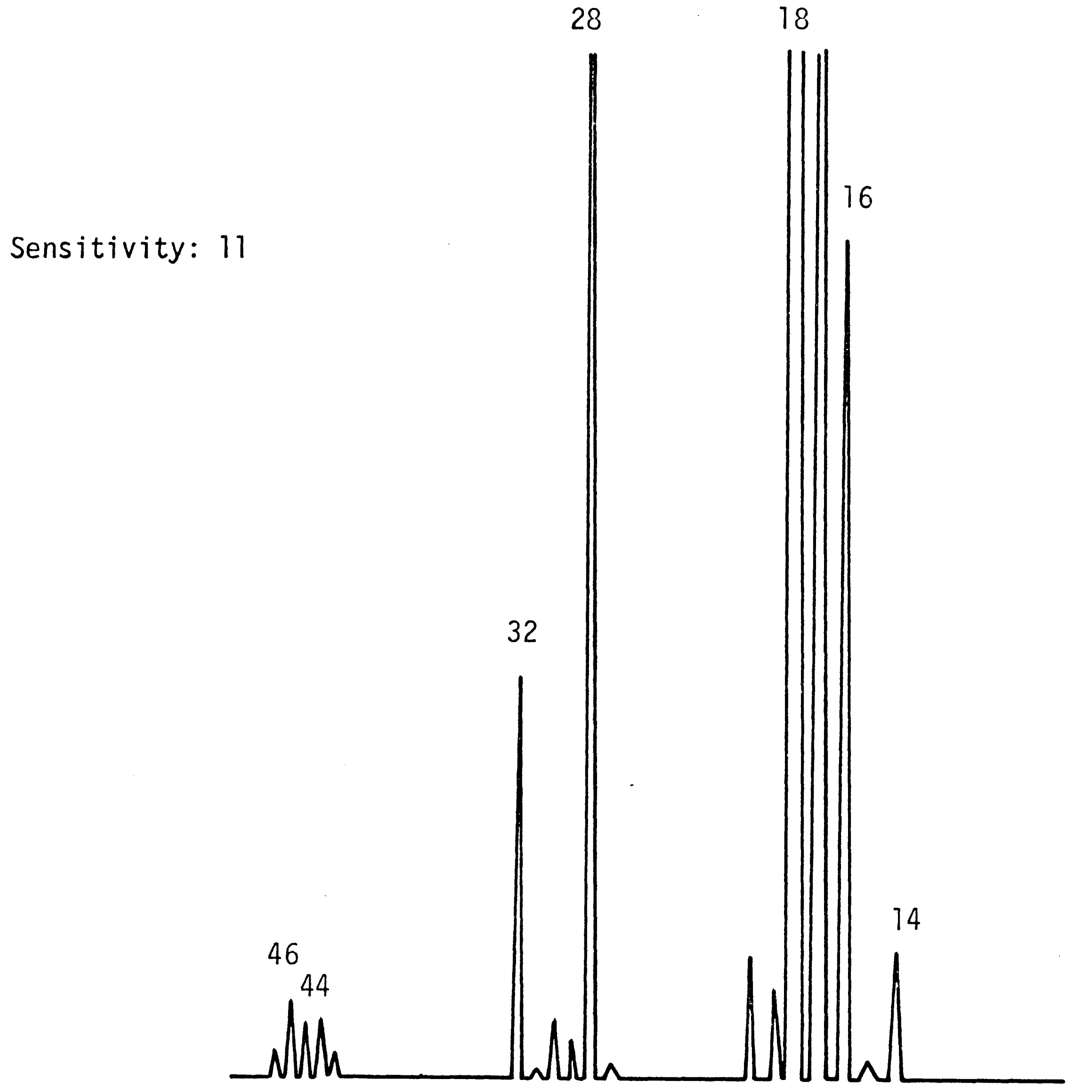


Figure 14 Mass Spectrum of Reaction Products of C_2H_2-O_2 Flame with 10 per cent Excess O_2. No Liquid N_2 in Reactor. Approximate temp. of Flame Holder: 23°C.

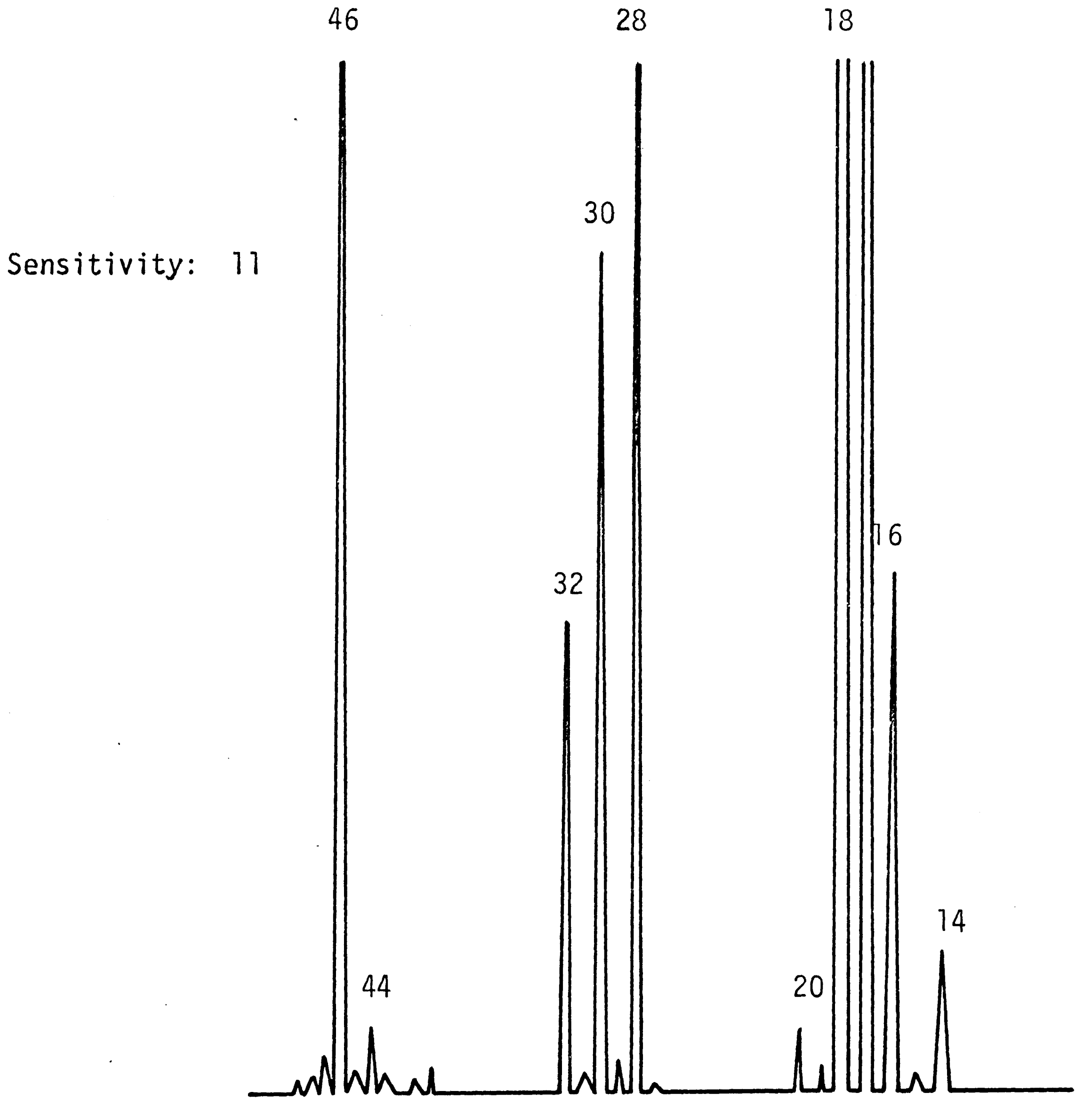


Figure 15 Mass Spectrum of Reaction Products of C_2H_2-O_2 Flame with 10 per cent Excess O_2. No Liquid N_2 in Reactor. Approximate temp. of Flame Holder: 146°C.

(Figures 16 to 18), (2) 10 per cent oxygen-rich (Figures 19 to 21), and (3) 10 per cent methane-rich (Figures 22 to 24). The mass spectra of the effluent product gases resembled those of the acetylene-oxygen system: at all three experimental conditions, no new or unusual compounds were observed. The same results were obtained with the popane-oxygen system with stoichiometric (Figures 25 to 27), 15 per cent oxygen-rich (Figures 28 and 29), and 15 per cent methane-rich mixtures (Figures 30 to 32). In these two systems, the bottom of the reactor was not heated after the reactor reached room temperature, thus no HNO_3 or H_2CO_3 were observed.

The results obtained from this work agree with the data published from a similar experiment in which a diffusion flame of acetylene was maintained beneath the surface of liquid air [29, 30] to give a solid containing mostly carbon with some CO_2 (or H_2CO_3), H_2O and HNO_3. At present, no information on submerged premixed flames is available to check the validity of the results of the present technique. However, one can refer to the work of Fristrom and his co-workers for an indirect comparison of the present work. Fristrom et al.[31, 32, 33, 34] used a different technique to study the premixed flames of hydrocarbons (CH_4, C_3H_8 and C_2H_2) and oxygen or air in which the composition of the flames was obtained by sampling the flame gases with a quartz microprobe and analyzing them with a mass spectrometer. The probe was designed so as to rapidly quench the sample by means of a quick drop in pressure and temperature; the quenching time was short compared to the half life of unstable species. Basically this quenching method used a rapid adiabatic expansion for cooling. Oxidant-rich flames were

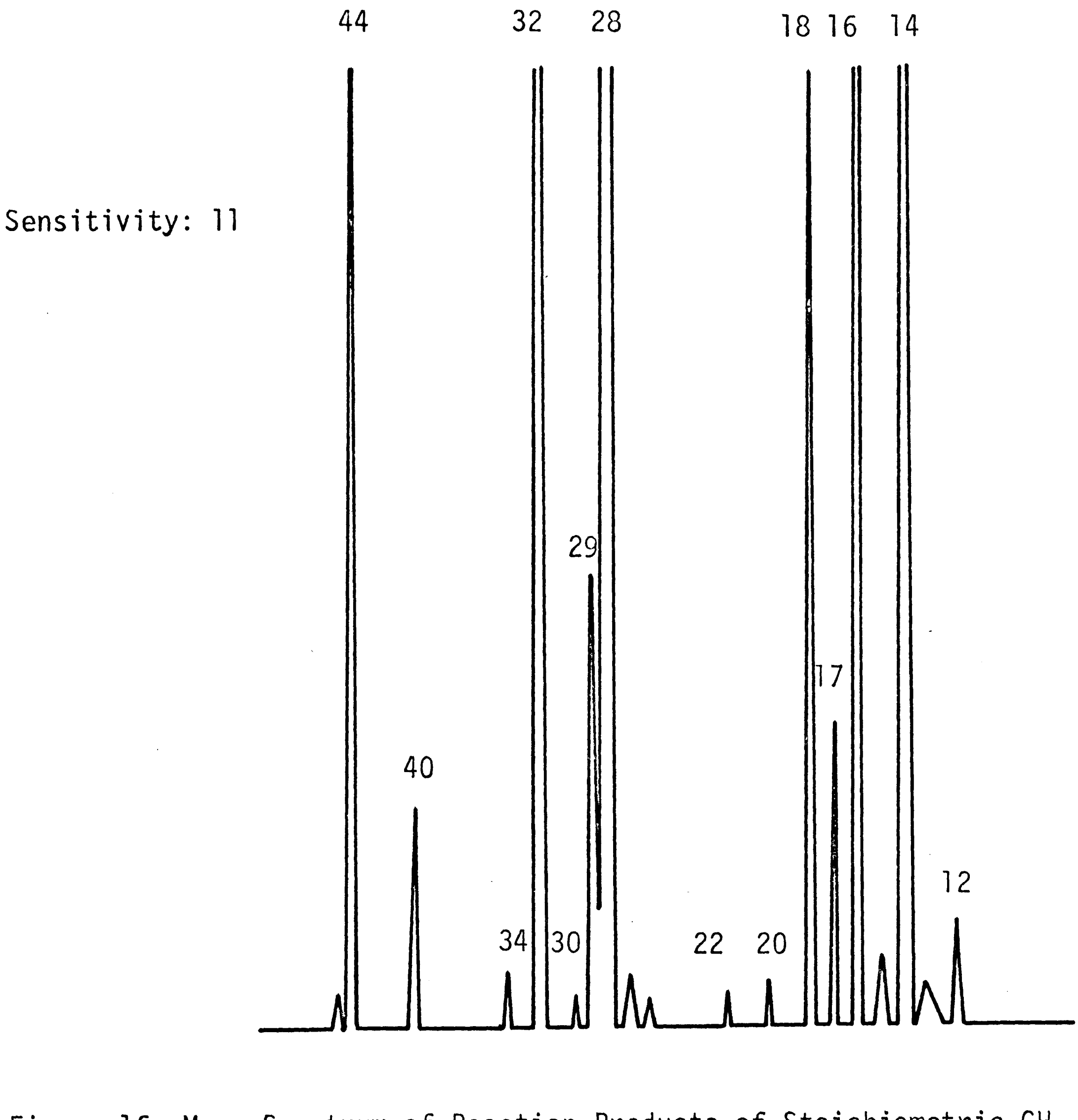


Figure 16 Mass Spectrum of Reaction Products of Stoichiometric CH_4-O_2 Flame. Liquid N_2 still Remaining in Reactor.

Sensitivity: 9

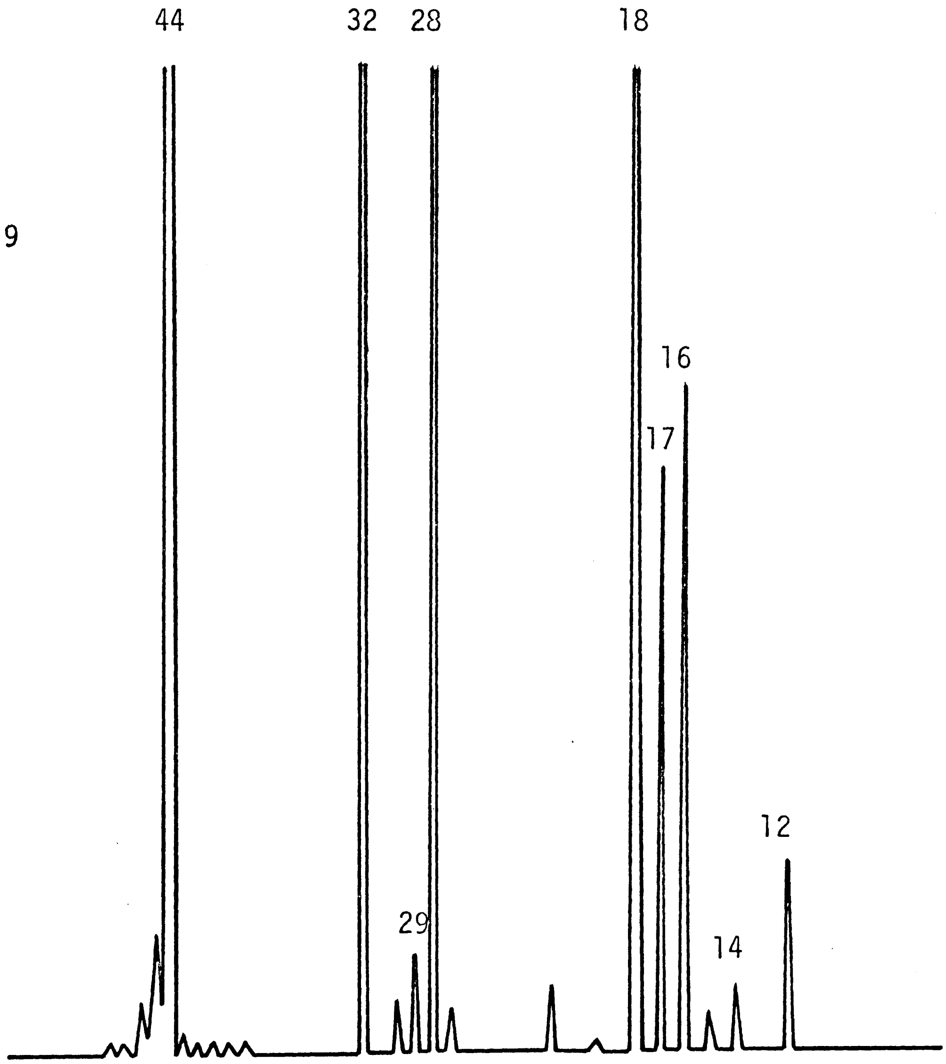


Figure 17 Mass Spectrum of Reaction Products of Stoichiometric CH_4-O_2 Flame. No Liquid N_2 in Reactor. Approximate temp. of Flame Holder: -192°C.

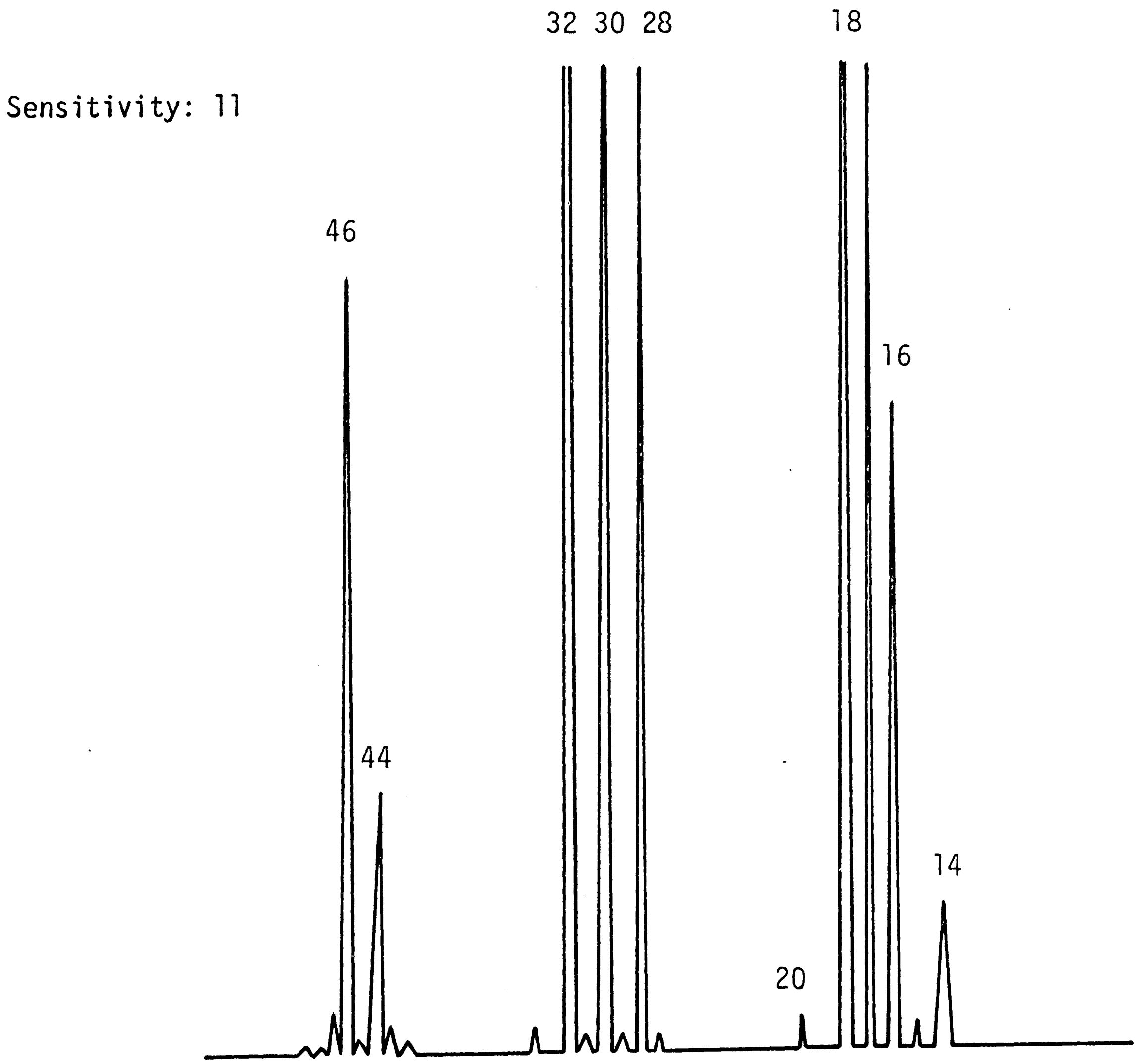


Figure 18 Mass Spectrum of Reaction Products of Stoichiometric CH_4-O_2 Flame. No Liquid N_2 in Reactor. Approximate temp. of Flame Holder: -106°C.

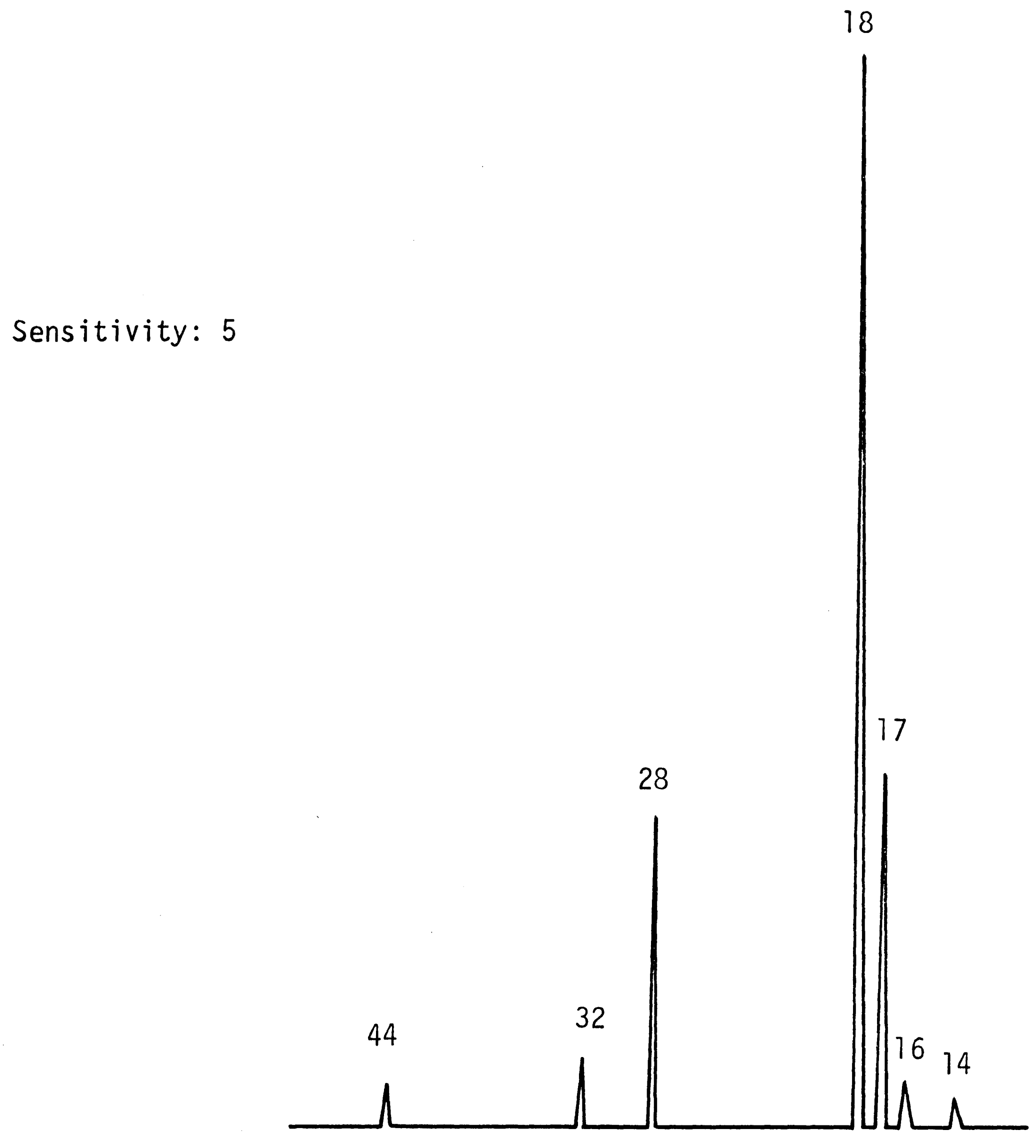


Figure 19 Mass Spectrum of Reaction Products of CH_4-O_2 Flame with 10 per cent Excess of O_2. No Liquid N_2 in Reactor. Approximate temp. of Flame Holder: -196°C.

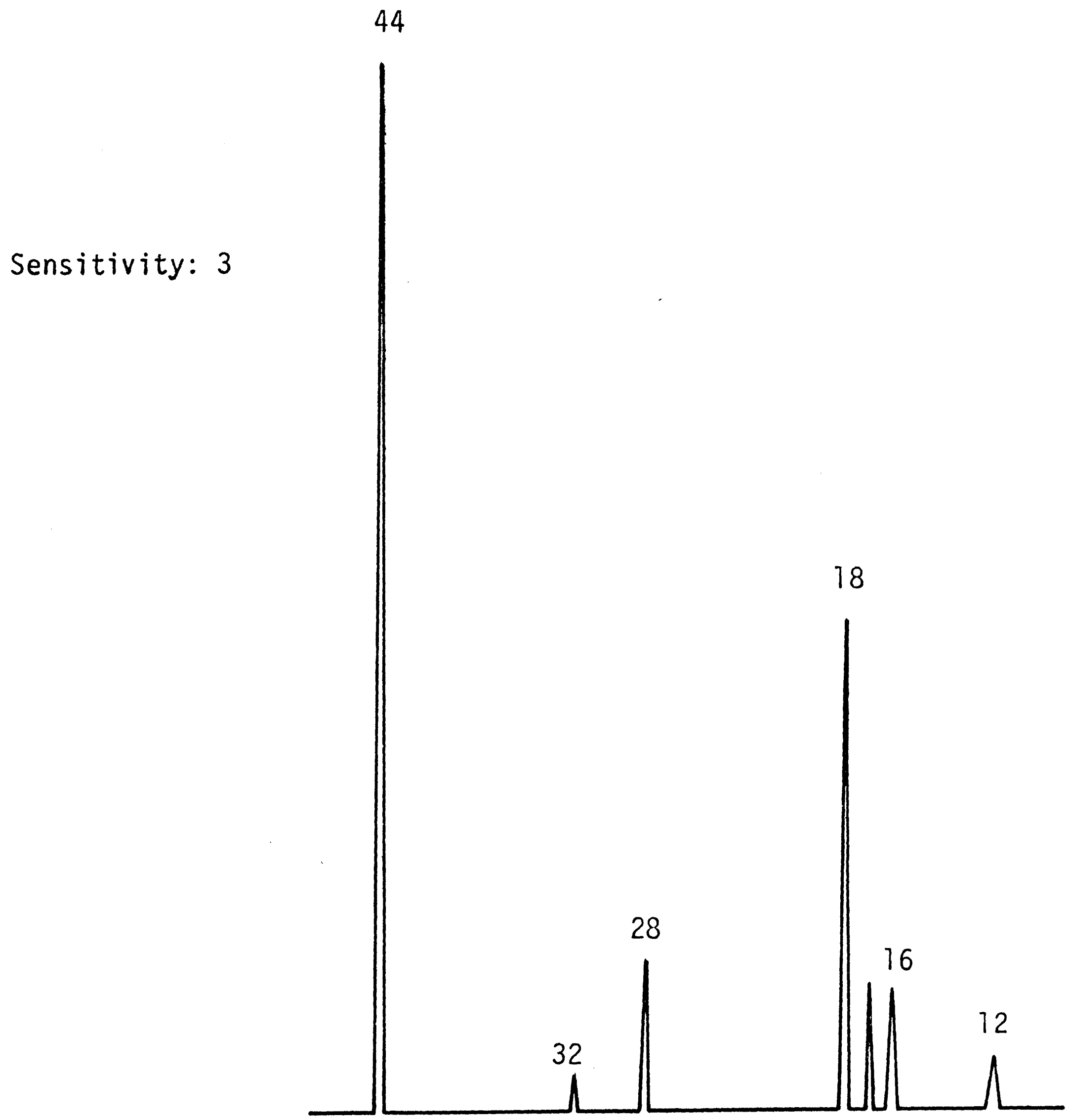


Figure 20 Mass Spectrum of Reaction Products of CH_4-O_2 Flame with 10 per cent Excess O_2. No Liquid N_2 in Reactor. Approximate temp. of Flame Holder: -164°C.

Sensitivity: 6

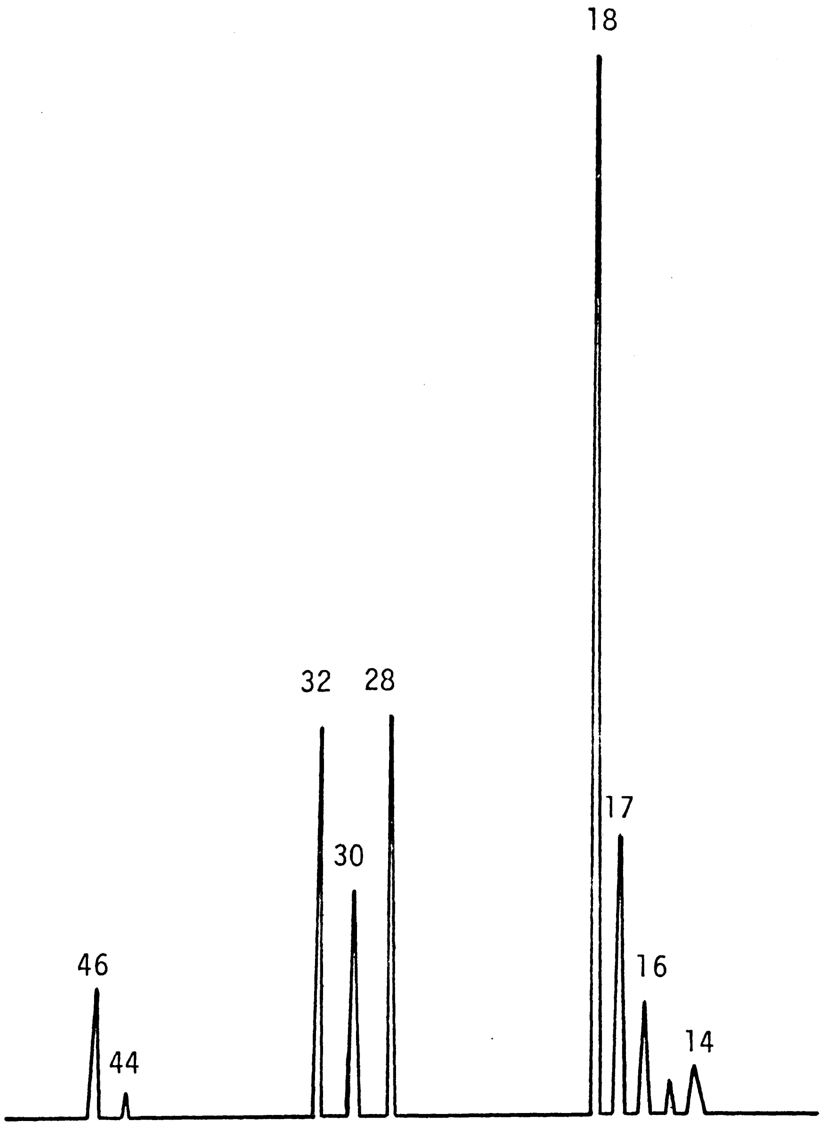


Figure 21 Mass Spectrum of Reaction Products of CH_4-O_2 Flame with 10 per cent Excess O_2. No Liquid N_2 in Reactor. Approximate temp. of Flame Holder: -106°C.

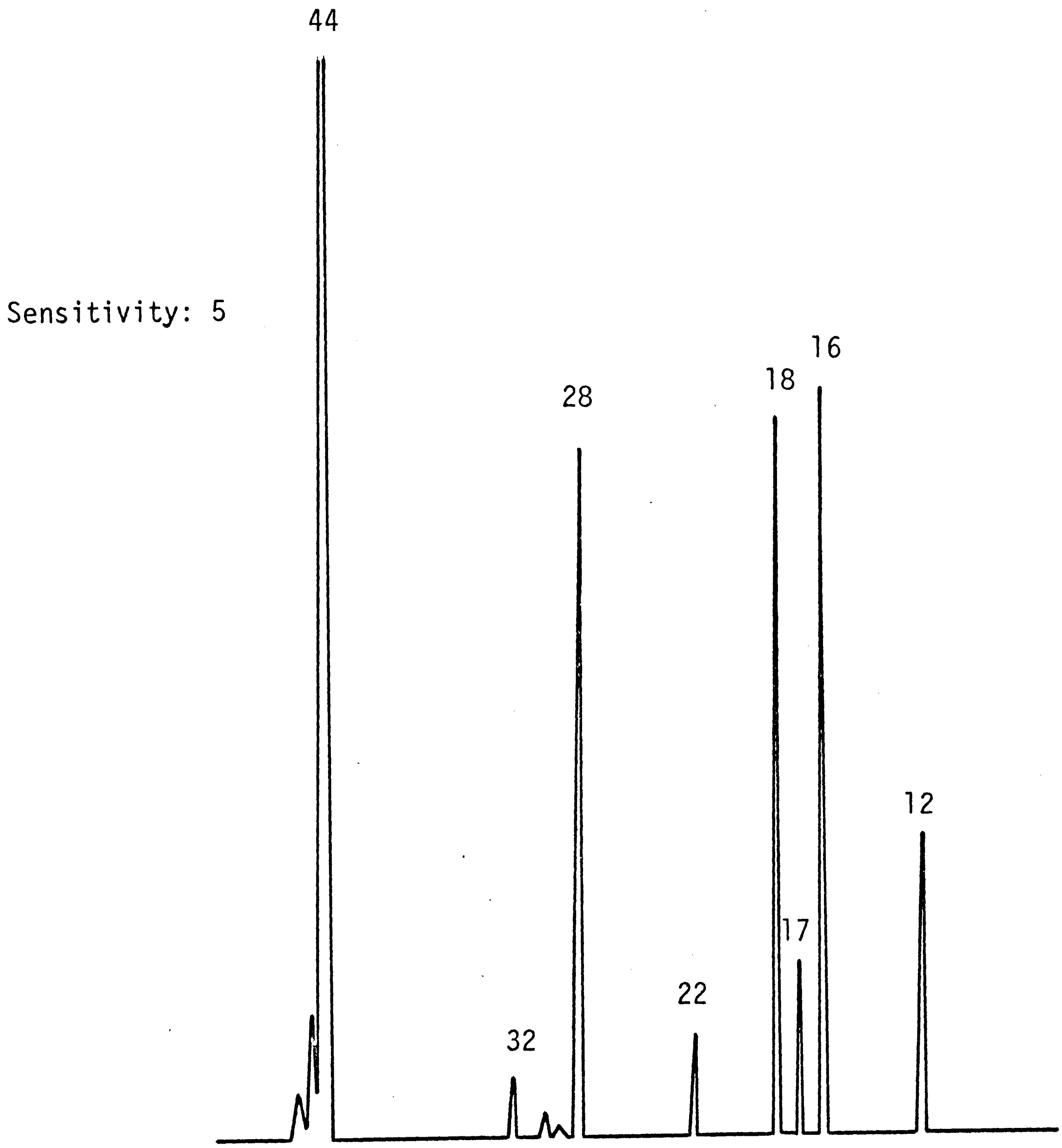


Figure 22 Mass Spectrum of Reaction Products of CH_4-O_2 Flame with 10 per cent Excess CH_4. No Liquid N_2 in Reactor. Approximate temp. of Flame Holder: -160°C.

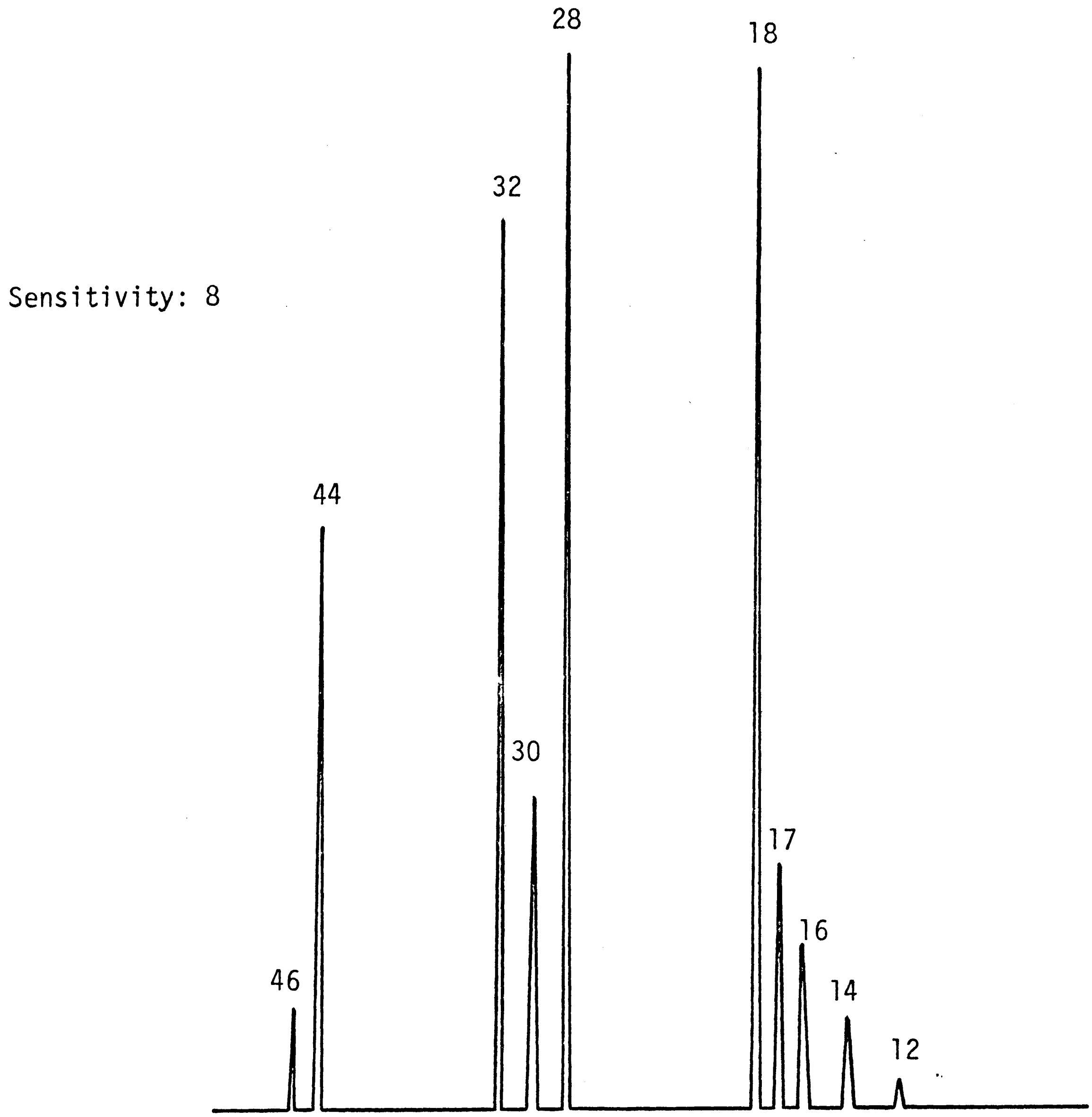


Figure 23 Mass Spectrum of Reaction Products of CH_4-O_2 Flame with 10 per cent Excess CH_4. No Liquid N_2 in Reactor. Approximate temp. of Flame Holder: -106°C.

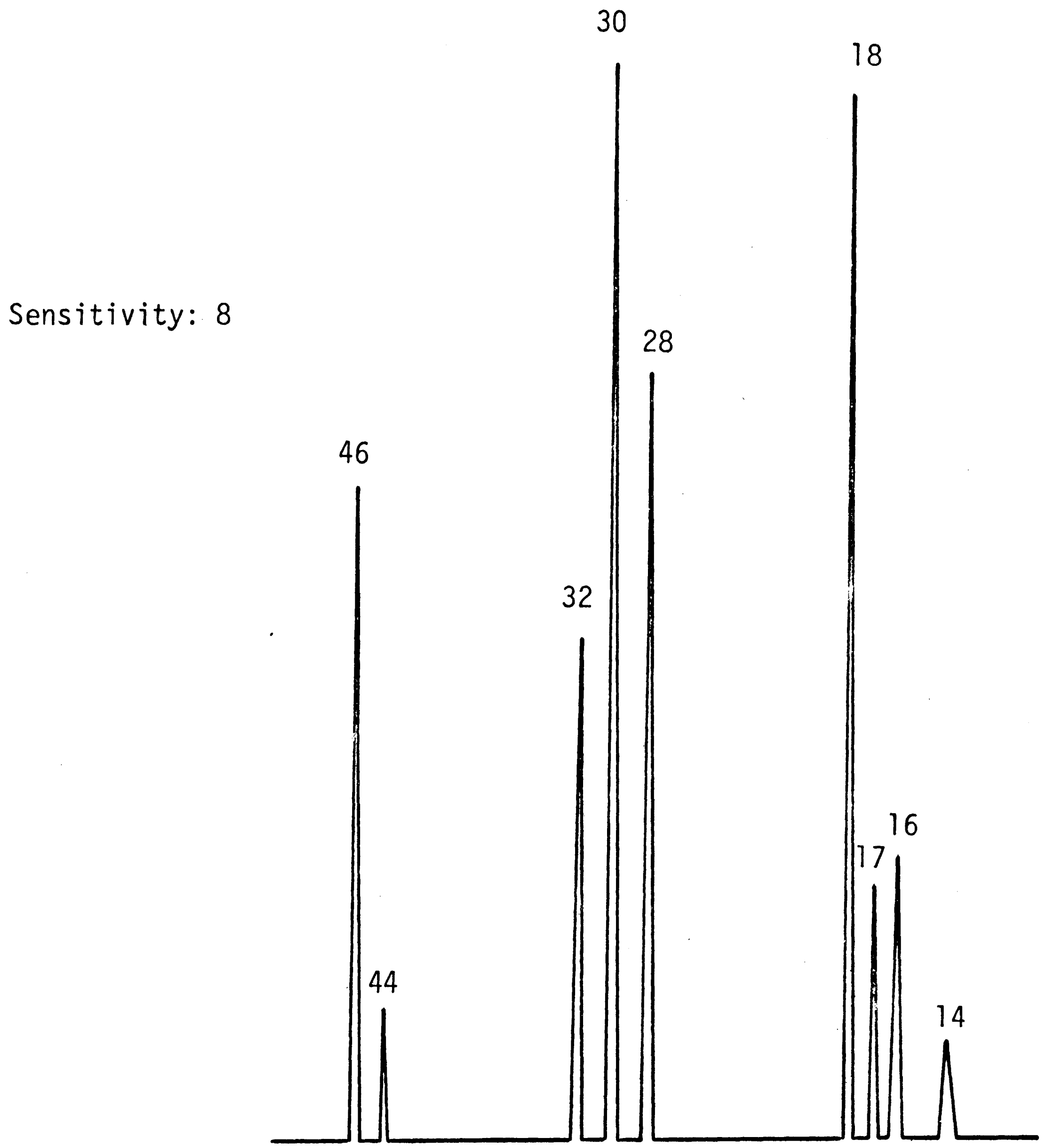


Figure 24 Mass Spectrum of Reaction Products of CH_4-O_2 Flame with 10 per cent Excess CH_4. No Liquid N_2 in Reactor. Approximate temp. of Flame Holder: -91°C.

Sensitivity: 6

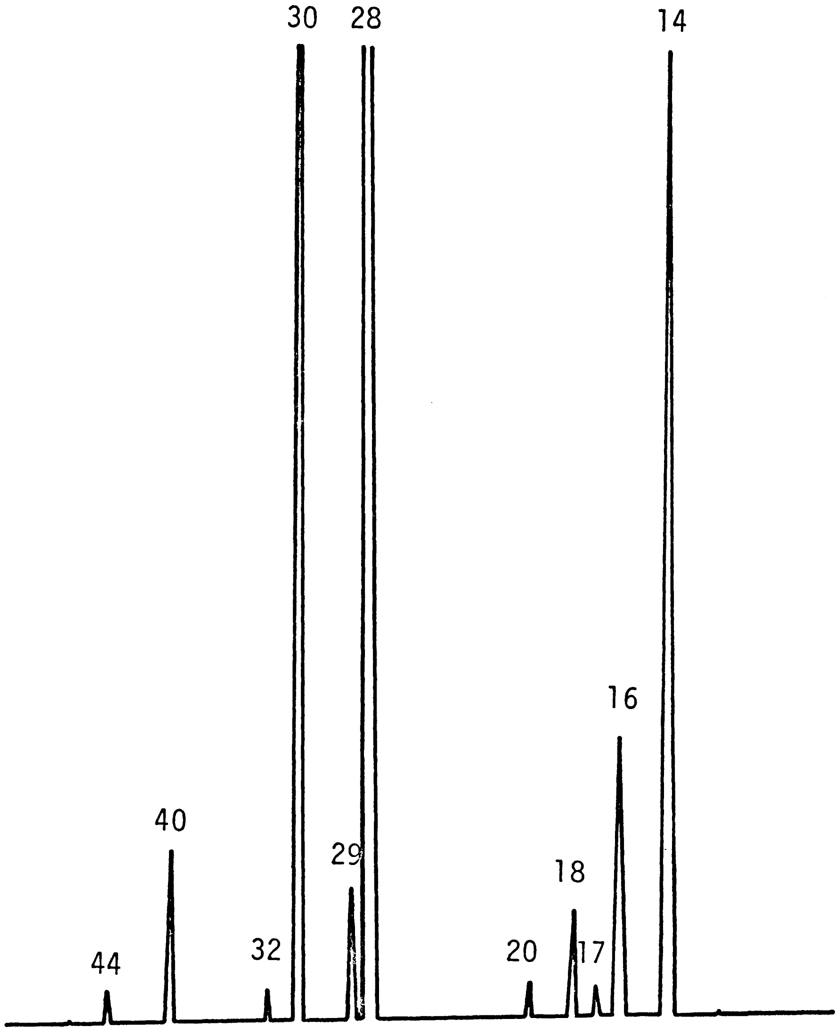


Figure 25 Mass Spectrum of Reaction Products of Stoichiometric C_3H_8-O_2 Flame. Liquid N_2 still Remaining in Reactor.

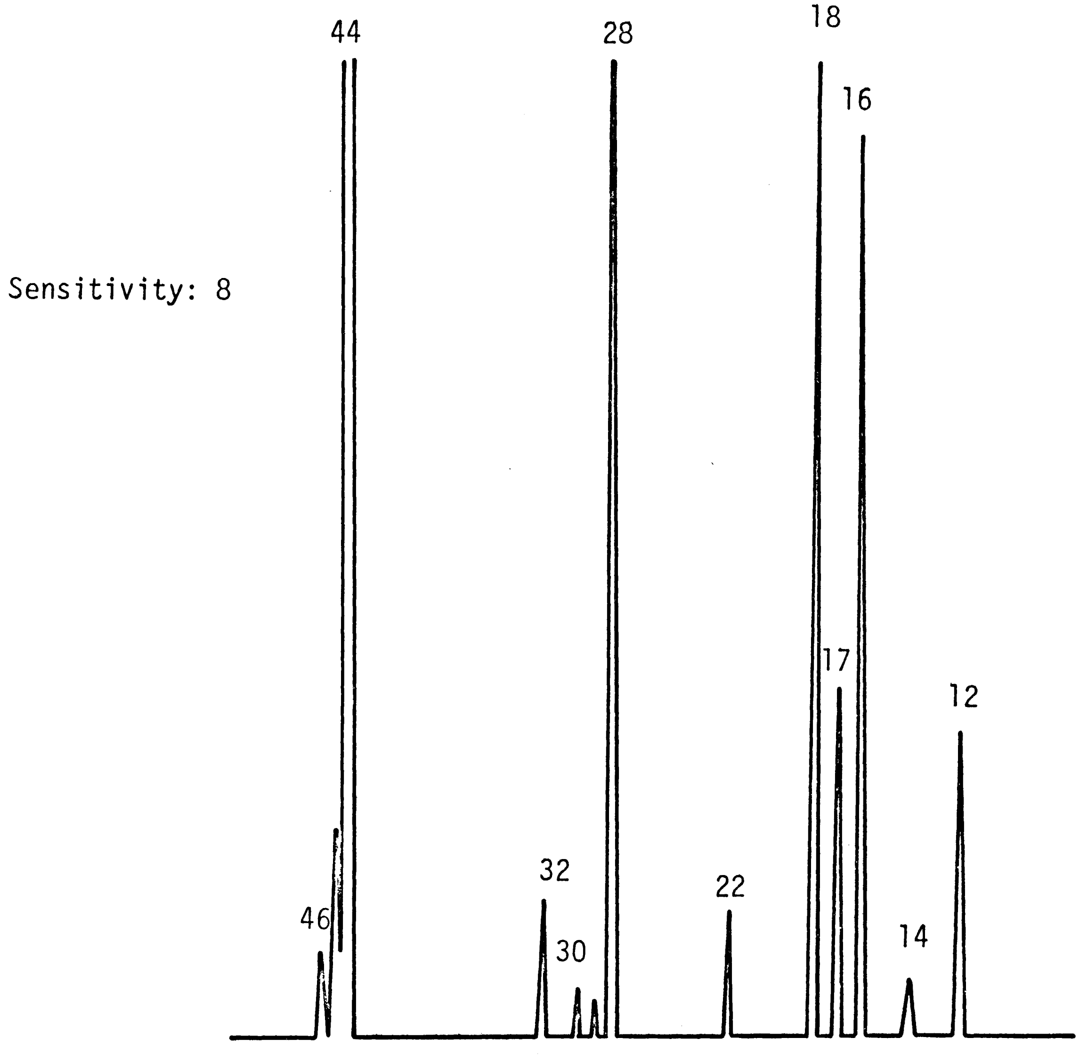


Figure 26 Mass Spectrum of Reaction Products of Stoichiometric C_3H_8-O_2 Flame. No Liquid N_2 in Reactor. Approximate temp. of Flame Holder: -186°C.

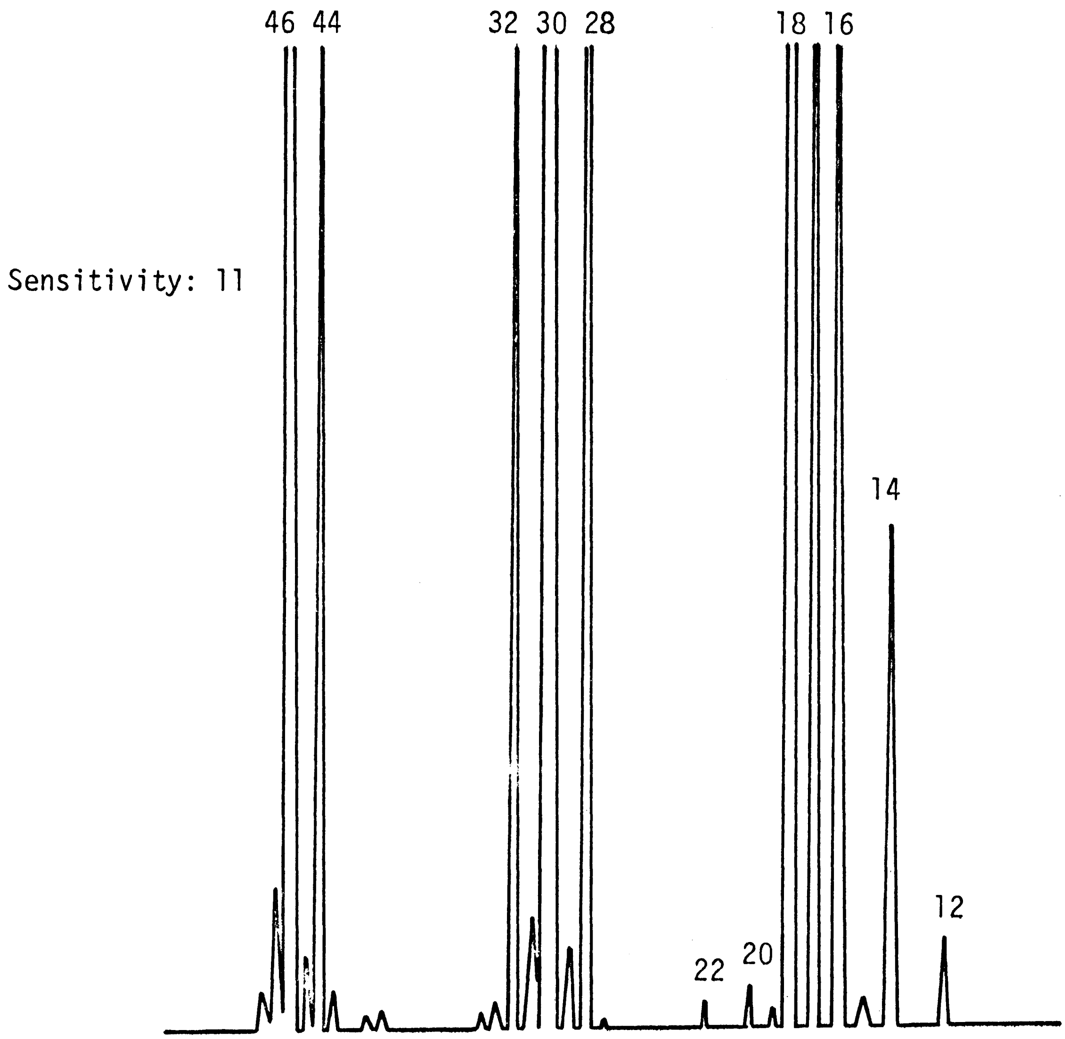


Figure 27 Mass Spectrum of Reaction Products of Stoichiometric C_3H_8-O_2 Flame. No Liquid N_2 in Reactor. Approximate temp. of Flame Holder: -88°C.

Sensitivity: 11

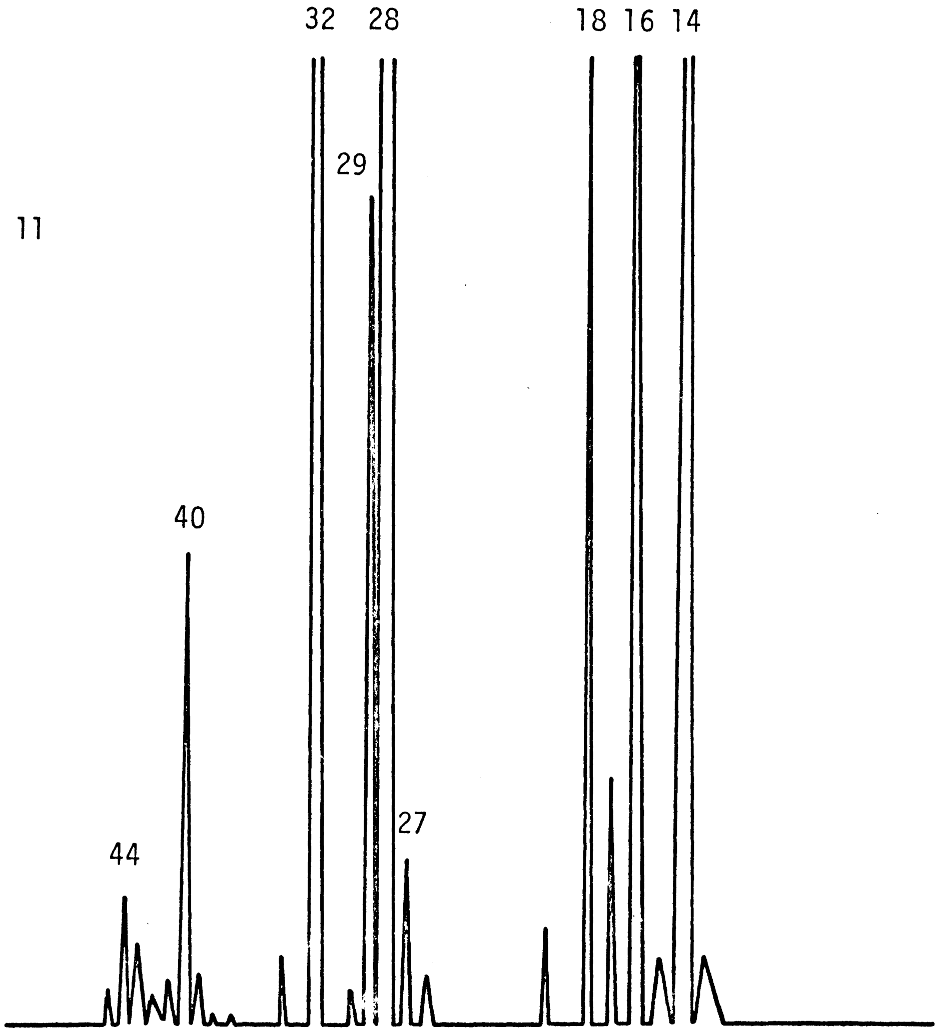


Figure 28 Mass Spectrum of Reaction Products of C_3H_8-O_2 Flame with 15 per cent Excess O_2. Liquid N_2 still Remaining in Reactor.

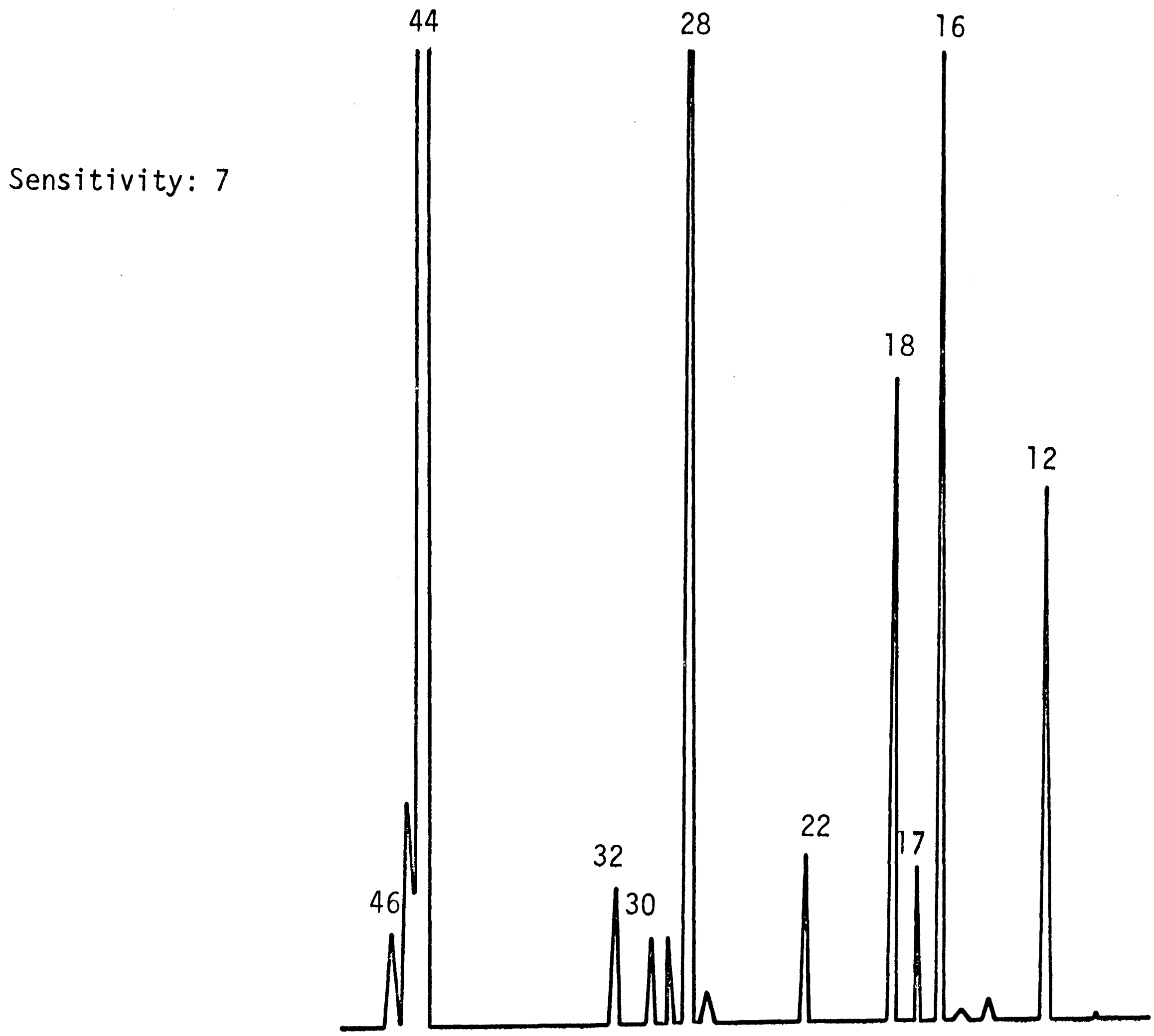


Figure 29 Mass Spectrum of Reaction Products of C_3H_8-O_2 Flame with 15 per cent Excess O_2. No Liquid N_2 in Reactor. Approximate temp. of Flame Holder: -169°C.

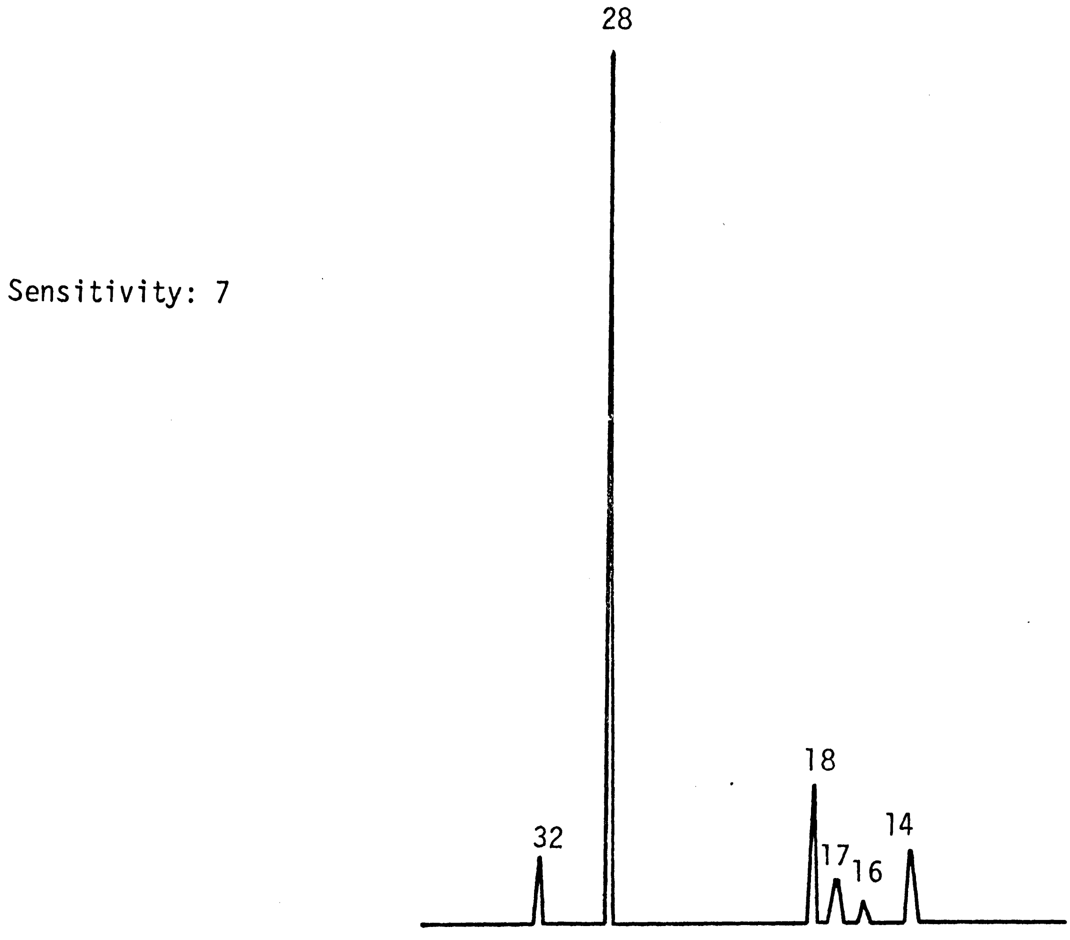


Figure 30 Mass Spectrum of Reaction Products of C_3H_8-O_2 Flame with 15 per cent Excess C_3H_8. Liquid N_2 still Remaining in Reactor.

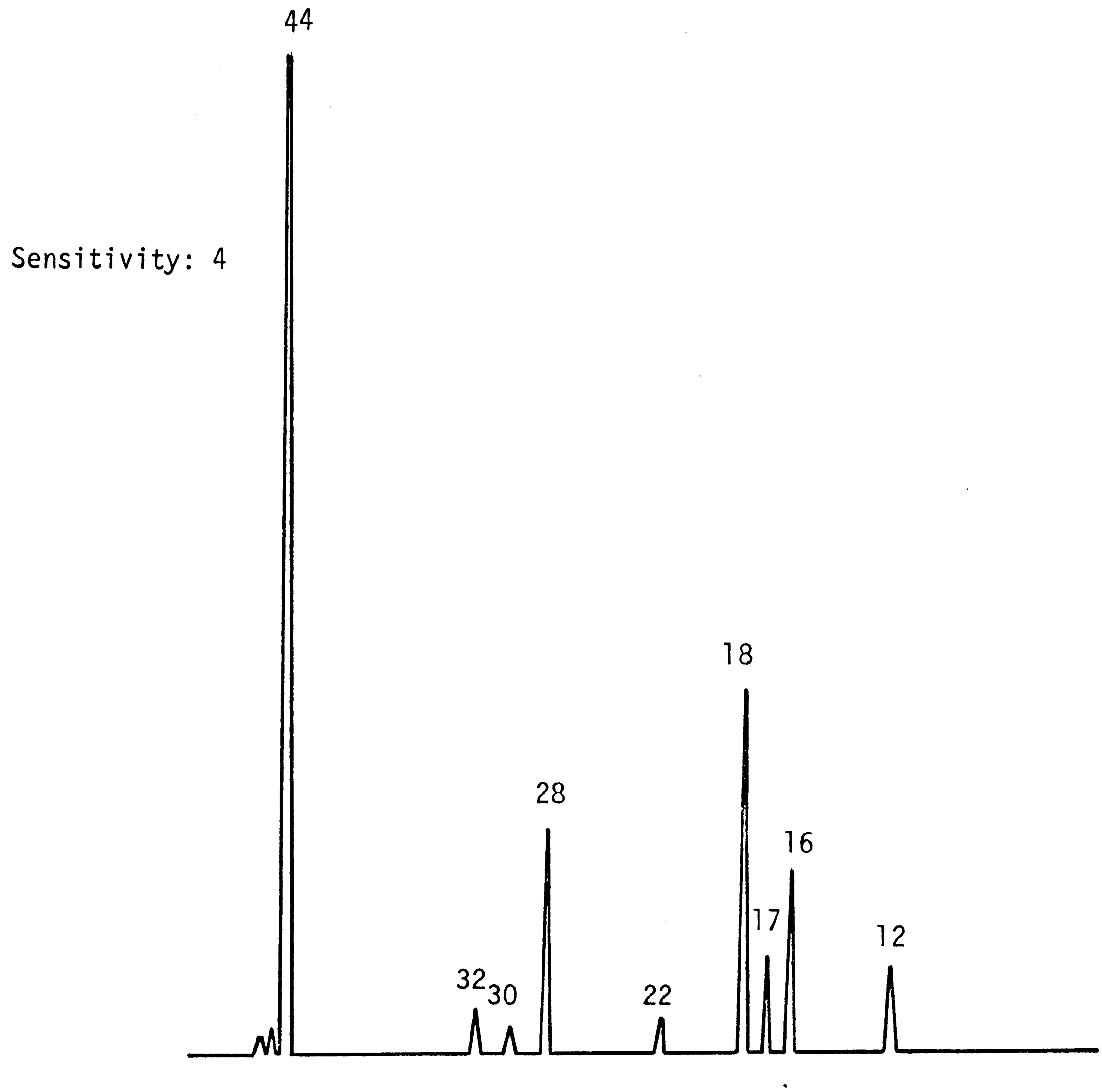


Figure 31 Mass Spectrum of Reaction Products of C_3H_8-O_2 Flame with 15 per cent Excess C_3H_8. No Liquid N_2 in Reactor. Approximate temp. of Flame Holder: -121°C.

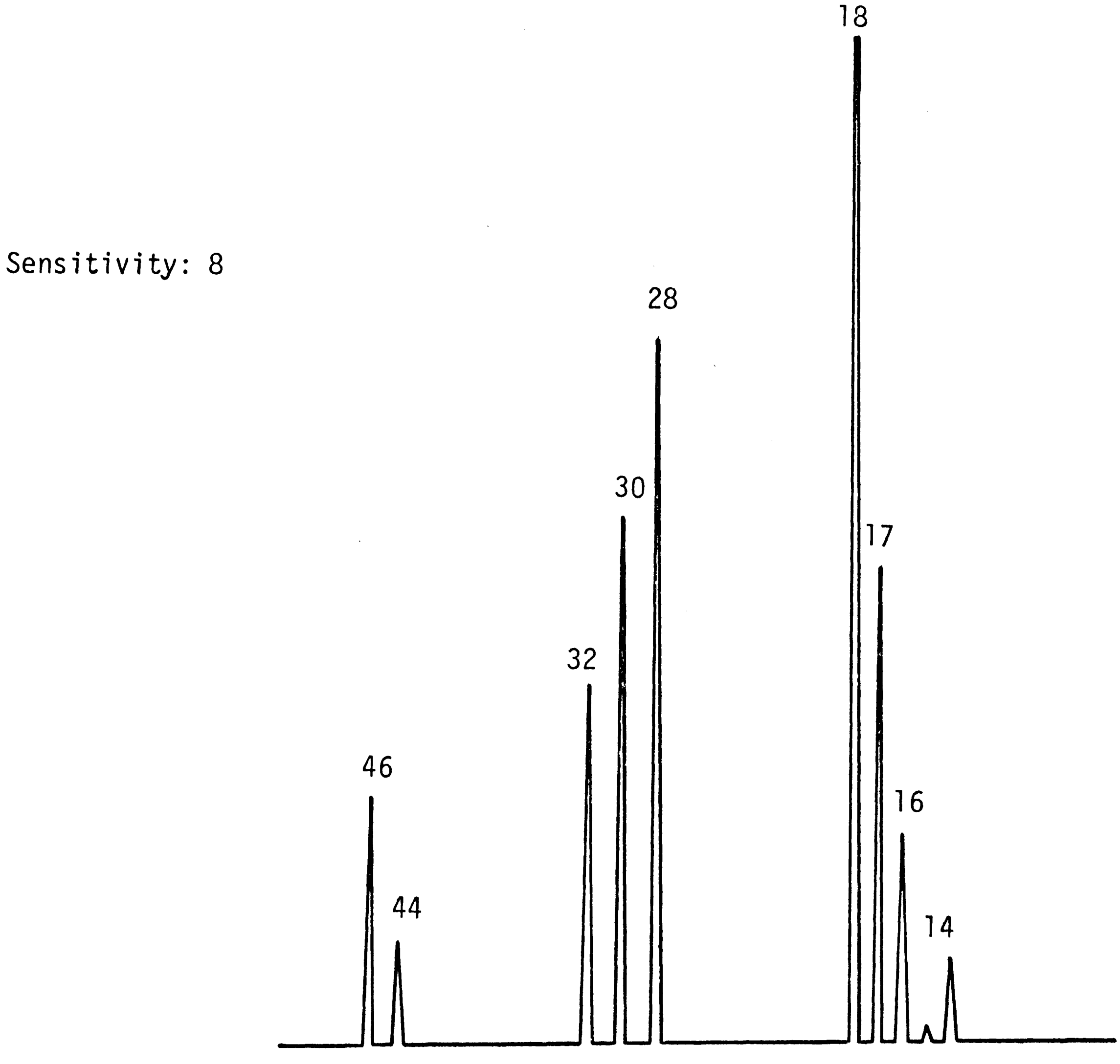


Figure 32 Mass Spectrum of Reaction Products of C_3H_8-O_2 Flame with 15 per cent Excess C_3H_8. No Liquid N_2 in Reactor. Approximate temp. of Flame Holder: -91°C.

chosen in these experiments so that the number of intermediates would be minimized. In fuel-rich saturated hydrocarbon flames, the concentration of hydrocarbon radicals is high enough for their recombinations to become important so that hydrocarbons of higher molecular weight than the original fuel are formed as intermediates, resulting in a more complex system for analysis.

Fristrom et al. found that fuel-lean premixed methane-oxygen flames contained five major stable species (CH_4, O_2, CO, CO_2 and H_2O) and two minor ones (H_2 and OCH_2) as opposed to twelve components found in the stoichiometric premixed propane-air flame (A, CO, CO_2, H_2, H_2O, N_2, CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_6 and C_3H_8). Several unsaturated propane derivatives appeared whereas no oxygenated molecules were observed. For a premixed oxygen-acetylene flame (oxygen-rich), the major constituents were C_2H_2, O_2, CO, CO_2 and H_2, and the minor ones, CH_4, OCH_2, and H_2. The absence of a number of intermediates was significant: hydrocarbons higher in molecular weight than acetylene, stable oxygen-containing compounds such as alcohols, aldehydes (except formaldehyde), acids, peroxy compounds, ozone and hydrogen peroxide. This present work does not give any clear evidence of the presence of some of the compounds that were observed by Fristrom and his co-workers. However, the absence of these compounds does not necessarily mean that their trapping by cryogenic means is unsuccessful. The possibility that these compounds are trapped but are not detected is argued in the following manner: due to a lack of the temperature control during the warm-up of the condensed products, the time interval between the evolution of the molecules is short, and, therefore, the separation of these compounds is obscured by the peak overlapping from one another.

A substantial presence of nitrogen oxides indicates that nitrogen atoms or molecules compete actively for oxygen atoms, and therefore, may to a great extent depress the formation of oxygenated products such as formaldehyde or methyl alcohol. This proposition can be verified under more controlled experimental conditions in which the proof of the absence or presence of the oxygen-containing compounds must be clearly shown. To conduct such an investigation, a modified reactor will be proposed and discussed in the Recommendations section of this thesis.

V. CONCLUSIONS

The results of the present work have led to the following conclusions:

(1) Observation port and inlet to the reactor must be made of Pyrex glass tube attached to the reactor with Kovar glass-to-metal seal to insure a leak proof system under vacuum at cryogenic temperatures. Pexiglass windows and adhesives such as epoxy or silicone rubber contracted and cracked on contact with liquid nitrogen or very cold surfaces.

(2) The use of the flame holder equipped with a variable heater to prevent the quenching of a submerged flame by a cold flame holder can be extended to other cryogenic fluids besides liquid nitrogen.

(3) The stoichiometric premixed hydrocarbons (CH_4, C_3H_8 and C_2H_2) -oxygen flames submerged in liquid nitrogen yielded condensed products which, when analyzed at room temperature, consisted of nitrogen oxides, carbon oxides, water and nitric acid (the presence of HNO_3 in the CH_4 and C_3H_8 flames was deduced from the observation of the C_2H_2 flame). The presence of NO_2, CO_2 and HNO_3 was clear, but the confirmation of NO and N_2O was equivocal due to the doubtful origin of the NO peak from the evolution of the two gases over a narrow temperature range; similarly, the detection of CO, CH_4 or OCH_2 was interfered by peak overlapping from other compounds.

(4) A 10 to 15 per cent deviation of either fuel or oxidant from the stoichiometry did not produce any change in the over-all chemistry that was observed.

VI. RECOMMENDATIONS

As an extension of the present work, the following recommendations are made:

(1) Due to the difficulty in identifying the source of the overlapping peaks, the warm-up of the condensed products inside the reactor should be conducted at a much slower rate so that the identification of each component can occur as each separately vaporizes at different temperatures depending on its relative volatility. Further analytical difficulties from overlapping vapor pressures can be overcome by measuring appearance potentials in addition to the evidence given by the mass spectral cracking patterns. In other words, the combined use of cracking pattern, relative volatility, and appearance potentials should be sufficient to identify the several species. To achieve this objective, a new design is suggested as is shown in Figure 33. In this new arrangement, the submerged combustion experiment will be carried out with the cylindrical reactor immersed in a cryogenic bath. Two advantages are obtained from this design:

a) Control of the warm-up rate of the reactor is essential. The walls of the reactor are in contact with the refrigerant in the bath, except for a part of the face at which the flame holder is attached. In this way, control of the gas evolution from the reactor can be regulated by gradually warming the refrigerant bath using an immersion heater and a stirrer. Such a refrigerant bath has been previously fabricated and used to carry out cryochemical reactions.[35] The basic design of this bath can be adapted to the present system as shown in

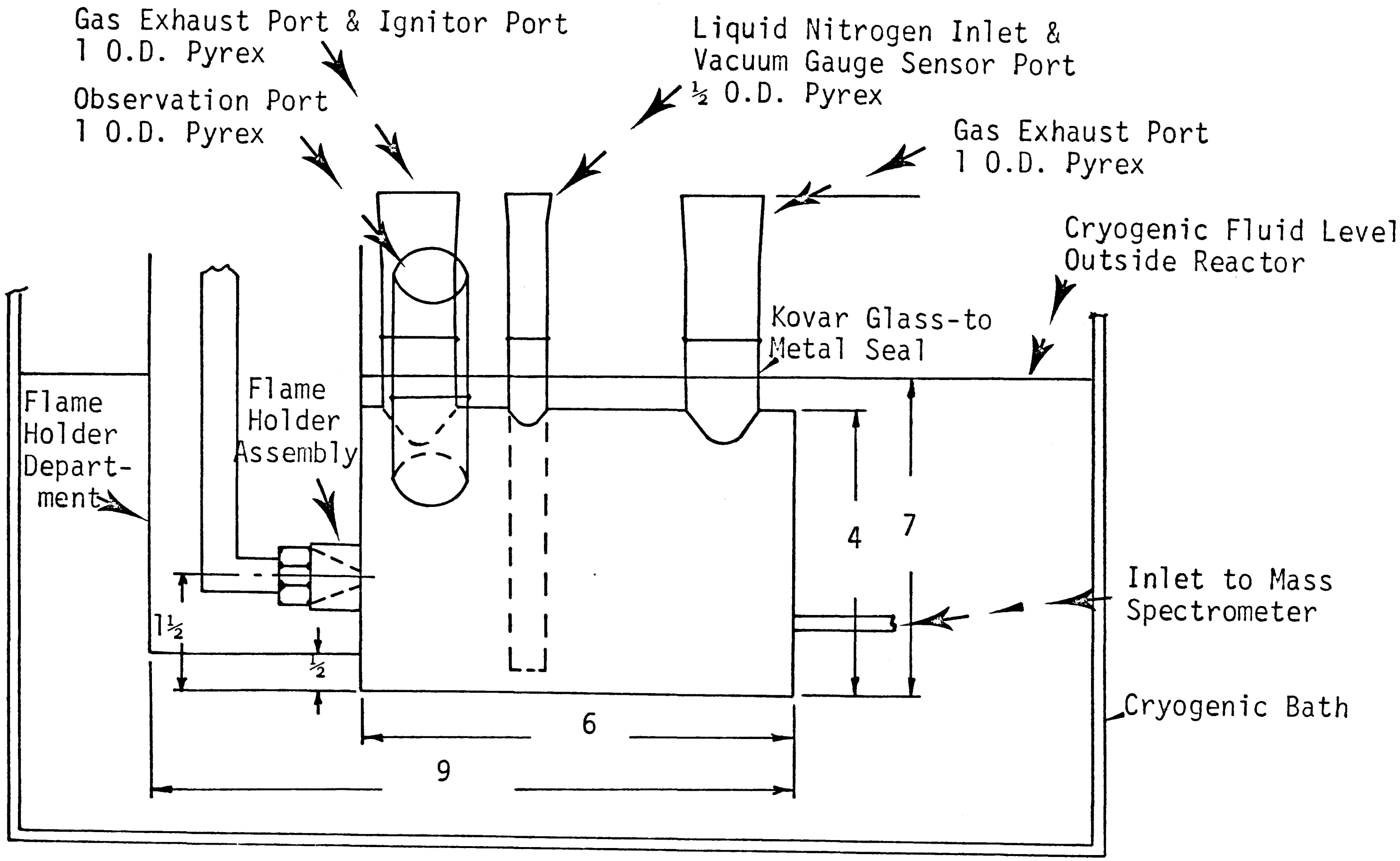


Figure 33 A Modified Cylindrical (4-inch dia.) Reactor for Submerged Combustion Experiments in a More Rigid Temperature Control Refrigerant. Only General Details and Dimensions Given. Heating Coil of the Flame Holder Not Shown.

Figure 34. The refrigerant itself is cooled by admitting liquid nitrogen into a coil immersed in the refrigerant bath.

The refrigerant should be liquid over a wide temperature range and should not be flammable, explosive or toxic. Hydrocarbon refrigerants, because of their flammable nature, cannot be used in this combustion work. The Freons are not flammable, explosive or toxic. Their useful normal freezing-boiling temperature ranges can be extended by using suitable mixtures.

b) A cryogenic product delivery line to the mass spectrometer is essential. In this way, the product delivery line of the reactor and the mass spectrometer inlet are both at the same temperature at which the condensed products inside the reactor vaporize. Thus, the possibility of product decomposition in the delivery line to the analytical instrument is almost nil. As shown in Figure 34 the refrigerant from the bath circulates through a cooling jacket around the entire length of the inlet tube by means of a pump. A glass wool filter prevents solid contaminants in the refrigerant from depositing in the pump. For ease of disassembly, a soft-soldered joint is recommended between the product delivery line of the reactor and the inlet line leading to the mass spectrometer inlet valve.

(2) A diffusion hydrocarbon flame can be studied with the second reactant, such as liquid oxygen, acting both as the refrigerant and the oxidant. The objective is to observe any difference in product formation between the premixed and diffusion flames. One would expect to obtain more oxygenated intermediates in a diffusion flame in liquid oxygen.

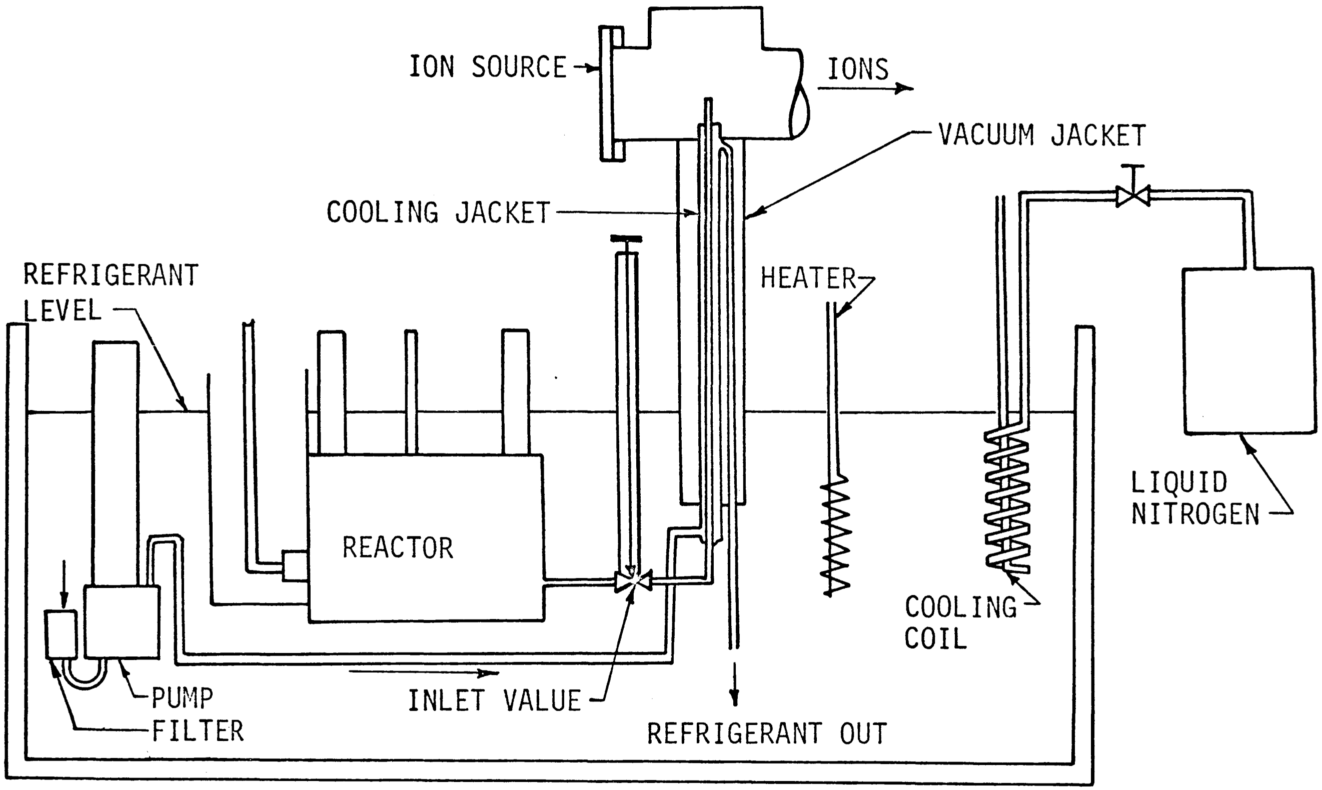


Figure 34. Refrigerant Temperature Regulation System.

VII. SUMMARY

In this exploratory work, several premixed flames were operated beneath the surface of liquid nitrogen in hopes that some unusual intermediates would be obtained from the resulting quenching process. This quenching would prevent the further reaction of the intermediates which would lead to the final products that are observed under more ordinary conditions.

The reactor consisted of a three-port cylindrical vessel with an observation port. The walls of the reactor were insulated from the ambient atmosphere with fiberglass and styrofoam. The flame was introduced into the reactor through a flame holder port in the center of the bottom of the reactor. Since a cold flame holder would quench a flame, it was equipped with a heater which could be controlled to keep the flame holder near room temperature even though it was submerged in liquid nitrogen.

Three premixed flames, CH_4-O_2, C_3H_8-O_2 and C_2H_2-O_2, were studied. The submerged stoichiometric combustion yielded condensed products, which, when mass spectrometrically analyzed at room temperature, consisted of nitrogen oxides, carbon oxides, water and nitric acid. The presence of NO_2, CO_2 and HNO_3 was clear, but the confirmation of NO, N_2O, CO, CH_4 or OCH_2 was somewhat equivocal due to overlapping peaks from several compounds. A 10 to 15 per cent deviation of either fuel or oxidant from stoichiometric mixture did not produce any change in the over-all chemistry that was observed.

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IX. APPENDIX A

This section contains the thermodynamic date required in the Sample Calculations section (Appendix B).

Heat Capacities

Gas. The mean heat capacity, $C_{p\ mean}$, of CO_2 (g) is desired in the temperature range of 298 to 195°K. From JANAF Thermochemical Tables,[36] the C_p values at 298°K and 200°K are respectively 8.874 cal/(g mole)(°C) and 7.734 cal/(g mole)(°C), thus the mean heat capacity, $C_{p\ mean}$, is 8.304 cal/(g mole)(°C).

Liquid. H_2O (l): $C_{p\ mean} = 1.0$ cal/(g)(°C)

Solids. CO_2 (s):[37] $C_p = 1.66 + 0.0048T$ in joules/(g)(°C) or $0.397 + 0.001145T$ in cal/(g)(°C) over a temperature range of 73-198°K.

H_2O (s):[38] $C_{p\ mean} = 0.511$ cal/(g mole)(°C) over a temperature range of 73-273°K. (The heat capacity of H_2O (s) is given in the Internation Critical Tables at some particular temperature over a wide temperature range. Thus the mean heat capacity is approximated as the weighted average over the desired temperature range.)

Heats of Combustion

The heats of combustion of CH_4, C_3H_8 and C_2H_2 are given below:[39]

$CH_4 + 2\ O_2 \rightarrow CO_2(g) + 2\ H_2O\ (l)$, $\Delta H°_{298} = -212{,}800$ cal

$C_3H_8 + 5\ O_2 \rightarrow 3\ CO_2(g) + 4\ H_2O\ (l)$, $\Delta H°_{298} = -530{,}600$ cal

$C_2H_2 + 2.5\ O_2 \rightarrow 2\ CO_2(g) + H_2O\ (l)$, $\Delta H°_{298} = -310{,}620$ cal

Heat of Sublimation of CO_2

Sublimation point at 1 atm. = 194.7°K

Heat of sublimation[40] = 36.2 cal/g

Heat of Vaporization of H_2O (l)

Heat of vaporization of H_2O (l)[41] = 10, 520 cal/(g mole)

Heat of Fusion of H_2O (s)

Heat of fusion of H_2O (s)[42] = 1, 436 cal/(g mole)

Heat of Vaporization of Liquid N_2

Normal boiling point = 77.4°K

Heat of vaporization [43] = 38.4 cal/cm^3

IX. APPENDIX B

This section contains sample calculations of the amounts of liquid nitrogen required to quench the combustion products to the boiling point of liquid nitrogen, 77°K.

Methane-Oxygen System

The combustion reaction at 298°K is written as:

$CH_4 + 2\ O_2 \rightarrow CO_2(g) + 2\ H_2O\ (1)$ $\Delta H°_{298} = 212{,}800$ cal

Basis: 15 mmoles/min CH_4 and 30 mmoles/min O_2

The paths of combustion products $CO_2(g)$ and H_2O (1) cooling from 298°K to 77°K are shown below:

$CO_2(g)$ @ 298°K		H_2O (1) @ 298°K	
↓	$Q_1 = C_{p\ mean}\ \Delta T$	↓	$Q_1 = C_{p\ mean}\Delta T$
$CO_2(g)$ @ 195°K		H_2O (1) @ 273°K	
↓	Q_2 = -Heat of sublimation	↓	Q_2 = -Heat of fusion
$CO_2(s)$ @ 195°K		H_2O (s) @ 273°K	
↓	$Q_3 = C_p\ \Delta T$	↓	$Q_3 = C_{p\ mean}\Delta T$
CO_2 (s) @ 77°K		H_2O (s) @ 77°K	

The heat given up by CO_2 in cooling from 298°K to 77°K is calculated as follows:

$$Q_1 = C_{p\ mean}\ \Delta T = (8.304)(195\text{-}298) = -855 \text{ cal/ g mole}$$

$$Q_2 = -\ (36.2 \text{ cal/g})(44\text{g/mole}) = -1{,}593 \text{ cal/g mole}$$

$$Q_3 = C_p\ \Delta T = \int_{195}^{77} (0.397 + 0.001145T)\ dT = -65 \text{ cal/g mole}$$

$$Q_{Total} = -(855 + 1{,}593 + 65) = -2{,}513 \text{ cal/g mole}$$

The heat given up by H_2O in cooling from 298°K to 77°K is calculated below:

$Q_1 = C_{p\ mean} = (1.0\ cal/(g)(°C)(18\ g/mole)(273-298) = -450\ cal/g\ mole$

$Q_2 = -1{,}436\ cal/g\ mole$

$Q_3 = C_{p\ mean} = (0.511)(77-273) = -100\ cal/g\ mole$

$Q_{Total} = -(450 + 1{,}436 + 100) = -\ 1{,}986\ cal/g\ mole$

For 15 mmoles/min of CH_4 and 30 mmoles/min of O_2, the net total heat given up by the combustion and the cooling of the combustion products from 298°K to 77°K at 1 atm. is computed as follows:

$$Q_{Net\ Total} = \underbrace{-212{,}800(15 \times 10^{-3})}_{\text{From combustion}} - \underbrace{2{,}513(15 \times 10^{-3})}_{\text{From cooling of } CO_2} - \underbrace{1{,}986\ (2)(15 \times 10^{-3})}_{\text{From cooling of } H_2O}$$

$$= 3{,}358\ cal/min$$

The rate of liquid nitrogen required to dissipate the net total heat given up is:

Rate of vaporization ofliquid nitrogen =

$$\frac{\text{Net total heat given up/min}}{\text{Heat of vaporization of liquid } N_2}$$

$$= \frac{3358\ cal/min}{38.4\ cal/cm} = 87\ cm^3/min \sim \underline{90\ cm^3/min}$$

<u>Propane-Oxygen System</u>

$C_3H_8 + 5\ O_2 \rightarrow 3\ CO_2(g) + 4\ H_2O\ (1) \qquad \Delta H°_{298} = -530{,}600\ cal$

Basis: 8.8 mmoles/min C_3H_8 and 43.9 mmoles/min O_2

The calculations of the net total heat given up by the combustion and by the cooling of the combustion products from 298°K to 77°k at

1 atm, are similar to the methane-oxygen system. The calculated rate of liquid nitrogen used by the propane-oxygen system is 130 cm^3/min.

Acetylene-Oxygen System

$C_2H_2 + 2.5\ O_2 \rightarrow 2\ CO_2(g) + H_2O\ (l) \qquad \Delta H°_{298} = -310{,}620$ cal

Basis: 17.4 mmoles/min of C_2H_2 and 43.6 mmoles/min of O_2

The calculated rate of liquid nitrogen used in this system is 140 cm^3/min.

IX. APPENDIX C

The vapor pressure data used int his work are listed in Table 6. The majority of the data are taken from the Chemical Engineer's Handbook.[44] Where required, extrapolation is made from the relationship of ln P (mm Hg) versus 1/T (K).

The compound identification by mass spectra was based on an eight-peak Mass Spectral Index (Table 7) compiled by Imperial Chemical Industries Ltd.[4-9]

Table 6. Temperature-Vapor Pressure Data Used in Identification of Reaction Products. Normal Melting and Boiling Points are also Included

Compounds	Temp. at which Products Exerted Vapor Press. of 1 mm Hg, °C	Melting Pt. at 1 Atm., °C	Boiling Pt. at 1 Atm., °C
CO	- 222.0	- 205.0	- 191.3
N_2	- 226.1	- 210.0	- 195.8
O_2	- 219.1	- 218.7	- 183.1
CH_4	- 205.9	- 182.5	- 161.5
NO	- 184.5	- 151.7	- 161.0
N_2O	- 143.4	- 90.9	- 85.5
CO_2	- 134.3	- 57.5	- 78.2
C_3H_8	- 128.9	- 187.1	- 42.1
NO_2	- 55.6	- 9.3	21.0
HNO_3 (anhydrous)	- 60.0 (extrapolated)	- 41.59 [45]	84.1 [46]
H_2O	- 17.0 [47]	0	100.0
HNO_3 (50% by weight)	40.0 [48]	———	———
OCH_2	- 88.0 @ 10 mm Hg	- 92.0	- 19.5

Table 7. Mass Spectral Data

	H_2O (18)						
m/e*	18	17					
Intensities	100	21					
	N_2 (28)						
m/e	28	14	29				
Intensities	100	5	1				
	O_2 (32)						
m/e	32	16					
Intensities	100	3					
	NO (30)						
m/e	30	14	15	16			
Intensities	100	8	2	1			
	N_2O (44)						
m/e	44	30	14	28	16	45	
Intensities	100	31	13	11	5	1	
	NO_2 (46)						
m/e	30	46	16	14			
Intensities	100	37	22	10			

* m/e = Mass to charge ratio.

Table 7. (cont'd) Mass Spectral Data

				CO (28)				
m/e*	28	12	16	14	29			
Intensities	100	5	2	1	1			
				CO_2 (44)				
m/e	44	28	16	12	22	45		
Intensities	100	7	5	2	1	1		
				CH_4 (16)				
m/e	16	15	14	13	12	17		
Intensities	100	86	17	9	3	1		
				C_2H_2 (26)				
m/e	26	25	24	13	27	12		
Intensities	100	20	6	6	3	3		
				C_3H_8 (44)				
m/e	29	28	27	44	43	39	41	26
Intensities	100	60	40	29	23	18	13	8
				OCH_2 (30)				
m/e	29	30	28	14	13	12	31	16
Intensities	100	86	31	4	4	3	2	2

*m/e = Mass to charge ratio.

IX. APPENDIX D

Materials

This section describes the materials used in this investigation.

Acetylene. 99.6 per cent minimum purity. Manufactured by Matheson Company. Used as a fuel in the submerged combustion experiment.

Liquid Nitrogen. Obtained from the Department of Physics, VPI &SU. Used as a cryogenic liquid to quench the combustion products from the combustion experiment.

Methane. 99 per cent minimum purity. Manufactured by Airco. Used as a fuel in the submerged combustion experiment.

Helium. 99.7 per cent minimum purity. Manufactured by Airco. Used to purge any build-up of fuel inside the reactor before each start of the combustion experiment.

Oxygen. 99.6 per cent minimum purity. Manufactured by Airco. Used as an oxidant in the submerged combustion experiment.

Propane. 99.5 per cent minimum purity. Manufactured by Phillips 66. Used as a fuel in the submerged combustion experiment.

Apparatus

This section describes the apparatus used in this investigation.

Asbestos Paper. Original source unknown. Obtained from the Chemical Engineering Laboratory, VPI & SU. Used as an electrical insulation between two electrical conductive surfaces (brass-nichrome and nichrome-nichrome) and also as a heat insulation material on the "hot" end of the flame ignitor to prevent scorching of the ignitor material from the flame when the gas mixture from the flame holder of the reactor is ignited.

Check Valves (2). Model 60-T on fuel line and Model 50-T on oxygen line. Manufactured by Victor company. Installed near the gas outlet end of the flow meter to permit gas flow in one direction.

Flame Holder. The flame holder was especially constructed around a nozzle, type OX-1, as described in details under the Flame Holder section in the Experimental chapter. The nozzle itself was manufactured by the National Welding Equipment Division, Veriflo Corporation, Richmond, California. Used to support a flame under liquid nitrogen.

Flame Ignitor. The flame ignitor basically consists of a heating coil of about seven inches of nichrome wire, 1.1 ohms per foot, wound in 5/32-inch diameter turns. The two ends of the heating coil are then connected to two copper wires leading to a variac. A detailed description is given under the Flame Ignitor section in the Experimental chapter. Used to ignite a gas mixture of fuel and oxygen flowing out of the flame holder.

Flow Meter (Gas, 2). Both 1/8-inch meters: model 448-210 on fuel line and model 448-211 on oxygen line. Manufactured by Fischer and Porter Company. Used to control the flow rates of gases to the mixing chamber. The calibration of these flow meters is given in the F & P handbook 10A9010.

Insulation Material. Fiberglass sheet. Specification unknown. Manufactured by Owens Corning Company. Obtained from the Chemical Engineering Stockroom, VPI & SU. Used to insulate the walls and the bottom of the reactor from ambient atmosphere.

Insulation Material. Styrofoam slab. Original source unknown. Obtained from the Chemical Engineering Stockroom, VPI & SU. Used as an outer layer of insulation after a first layer of insulation of Fiberglass for the walls of the reactor.

Mass Spectrometer. Time-of-flight. Model 14-107. Manufactured by Bendix Corporation. Used to analyze the product gases at room temperature from the evolution of the condensed products during the warm-up of the reactor.

Mass Spectrometer Recorder. Model 906 C Visicorder. Made by Honeywell Company. Used to record the mass cracking pattern from the mass spectrometer by means of a moving light tracing on a light sensitive photographic paper.

Mixing Chamber. The mixing chamber itself is the handle of the hand torch, model no. 3-A Blowpipe with a Koolite handle. Manufactured by the National Welding Equipment Division, Veriflo Corporation, Richmond, California. The fuel and oxygen flow into the handle and are mixed before they reach the nozzle (flame holder).

Heating Coil. Nichrome wire is used to make heating coil. Specifications: size B & W 22, 1.1 ohms per foot. Manufactured by Driver-Harris Company, Harrison, New Jersey. Heating coil is used to maintain the flame holder warm when the combustion experiment is carried under liquid nitrogen (see under the Flame Holder section in the Experimental chapter for more details).

Oscilloscope. Cathode-ray type, model 543-A. Manufactured by Tektronic, Inc., Beaverton, Oregon. Used to visually display the mass cracking pattern of the mass spectrometer.

Photographic Paper. Type 1895, standard size: 6 in. x 100 ft. Manufactured by Eastmen Kodak Company, Rochester, New York. Used in the mass spectrometer recorder to record the mass cracking pattern.

Pressure Regulator (Acetylene and Propane). Stock no. 806-8132, single-stage regulator with a needle valve, two pressure gauges: 400 and 60 psi maximum, CGA no. 510. Manufactured by Airco, Union, New Jersey. Used to regulate the flow rates of fuel going to the flow meter.

Pressure Regulator (Helium). Model 9, two-stage regulator with a needle valve, two pressure gauges: 3,000 and 400 psi maximum. Used to regulate helium flow rates. Helium was used to purge the inside of the reactor for any build-up of fuel before the start of a combustion experiment.

Pressure Regulator (Methane). Stock no. 806-8403, two-stage regulator with a needle valve, two pressure gauges: 3,000 and 60 psi maximum, CGA no. 350. Manufactured by Airco, Union, New Jersey. Used to regulate methane flow rates to the flow meter.

Pressure Regulator (Oxygen). Stock no. 806-9106, single-stage regulator with a needle valve, two pressure gauges: 400 and 200 psi maximum, CGA no. 540. Manufactured by Airco, Union, New Jersey. Used to regulate oxygen flow rates to the flow meter.

Pumps (2). Welch Duo-Seal mechanical vacuum pumps, model 1405 B, 1/2 h.p., free air displacement of 58 liters/min. Manufactured by the Welch Scientific Company, Skokie, Illinois. Used to evacuate nitrogen and combustion gases inside the reactor to vacuum condition before it is connected to the mass spectrometer.

Reactor. See under the Reactor section in the Experimental chapter.

Vacuum Gauge Sensor. Thermocouple gauge sensor, type DV-1M, connected to a control unit, model no. DG 2-2T with a vacuum range of 1 to 10^{-3} torr. Manufactured by Vacuum-Electronics Corporation (Veeco), Plainview, Long Island, New York. Used to measure the vacuum inside the reactor.

Variacs (2). Variable autotransformer, model 116 B, 120 volts, ac, 50/60 cycles, 10 amps, 1 kva. Manufactured by Superior Electric Company, Bristol, Connecticut. One variac was used to control the power input to the heating coil of the flame holder, the other, to control the power input to the flame ignitor.

Temperature Indicator. Potentiometer type, model unknown, serial no. 89571. Manufactured by Leeds and Northrup Company, Philadelphia, Penn. Used with a copper-constantan thermocouple (embedded between layers of asbestos paper wrapped around the brass cylinder of the flame holder) to measure the approximate temperature of the flame holder.

Tubing. Tygon tubing, Formulation no. R 3603, 1/4-inch inside diameter. Manufactured by Fisher Scientific Company. Used as gas flow line.

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SUBMERGED COMBUSTION OF PREMIXED HYDROCARBON-OXYGEN FLAMES IN LIQUID NITROGEN

by

(Mike) Ngoc Le-Si

(ABSTRACT)

In this exploratory work, several premixed flames were operated beneath the surface of liquid nitrogen in hopes that some unusual intermediates would be obtained from the resulting quenching process. This quenching would prevent the further reaction of the intermediates which would lead to the final products that are observed under more ordinary conditions.

The reactor consisted of a three-port cylindrical vessel with an observation port. The walls of the reactor were insulated from the ambient atmosphere with fiberglass and styrofoam. The flame was introduced into the reactor through a flame holder port in the center of the bottom of the reactor. Since a cold flame holder would quench a flame, it was equipped with a heater which could be controlled to keep the flame holder near room temperature even though it was submerged in liquid nitrogen.

Three premixed flames, CH_4-O_2, C_3H_8-O_2, and C_2H_2-O_2, were studied. The submerged stoichiometric combustion yielded condensed products, which, when mass spectrometrically analyzed at room temperature, consisted of nitrogen oxides, carbon oxides, water and nitric acid.

The presence of NO_2, CO_2 and HNO_3 was clear, but the confirmation of NO, N_2O, CO, CH_4 or OCH_2 was somewhat equivocal due to overlapping peaks from several compounds. A 10 to 15 per cent deviation of either fuel or oxidant from stoichiometric mixture did not produce any change in the over-all chemistry that was observed.