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An Experimental Study of the Sensitiveness of Unconfined Hydrocarbon-Air Mixtures to Direct Detonative Initiation

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(6) AN EXPERIMENTAL STUDY OF THE SENSITIVENESS OF UNCONFINED
HYDROCARBON-AIR MIXTURES TO DIRECT DETONATIVE INITIATION

by

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SUMMARY   (14) PERME-TR-44

An experimental technique is described whereby the sensi-
tiveness of a number of hydrocarbon/air mixtures is assessed
in terms of direct detonative initiation from solid explosive
charges. A microwave interferometer is used to monitor continu-
ously the propagation of the reaction zone in the gaseous system
over a path length of several metres, and to give a reliable
distinction between detonation and deflagration. The hydro-
carbons acetylene, ethylene, ethane, propane, butane, isobutane,
and methane are ranked in order of the sensitiveness of the
stoichiometric fuel/air mixtures. The critical initiation energy
of ethane is measured as a function of fuel/air stoichiometry.
Ethane, the most abundant "impurity" in natural gas, turns out
also to be the most sensitive; the minimum initiation energy
for various stoichiometric methane/ethane/air is assessed. A
brief literature survey is included.

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1   INTRODUCTION

Over recent years there has been a considerable growth in potential hazards arising from an increase in the occurrence of accidental release or spillage of large quantities of explosive vapours and gases. The necessity to transport and store ever increasing quantities of hydrocarbon fuels has excited a revival of interest in the study of the fundamental mechanisms involved in the initiation and propagation of unconfined explosions and detonations in fuel/air mixtures.

Depending on the nature of the ignition source, combustion of a flammable fuel/air mixture will be either deflagrative or detonative. Ignition studies relating to fuel/air mixtures indicate that initiation of a deflagration wave is much easier than direct initiation of a detonation wave; typically a deflagration may be initiated in a hydrocarbon/air mixture with a spark energy of less than a millijoule, whereas direct initiation of a detonation wave will require an energy deposition of several thousand joules. Therefore, in the accident situation deflagration is more likely to occur. There is no doubt, however, about the occurrence of detonations in unconfined vapour-cloud explosions, although firm proof is lacking in the accident environment, as such explosions are never instrumented. The direct initiation of a detonation by a sufficiently strong ignition source is not the only mechanism by which a self-sustaining detonation wave may be established, there is also the possibility of the transition of a deflagration into a detonation by flame acceleration processes. The mechanism of flame acceleration processes is not fully understood at present, in spite of extensive studies both in tubes and in an unconfined geometry, and is not the subject of this report, which confines its attention solely to the case of direct initiation of spherical detonation waves.

Experimental data on the direct initiation of fuel/air detonations in an unconfined geometry is somewhat sparse, particularly in the case of the less "sensitive" fuels such as methane, since the large ignition energies and volumes of explosive gaseous mixtures involved are not compatible with laboratory-scale investigations; indeed a number of large-scale experiments aimed at studying spherical detonations may be criticised on the grounds that the volumes of gas used were insufficient to establish unequivocally the existence of stable detonative propagation.

The instrumented bomb chambers at PERME, which are suitable for firing explosive charges of up to 3 kg of TNT, have afforded an ideal experimental

environment for the study of the initiation and propagation of spherical detonation waves in gas volumes of up to 2 cubic metres. It will be shown in this report that this facility has enabled a reliable assessment of the relative sensitiveness of a number of hydrocarbon fuel/air mixtures to be made in the context of direct detonative initiation, and has also assisted in the elucidation of the mechanism of initiation and propagation of spherical detonation waves.

The report aims principally at describing the experimental techniques used to assess the detonability of fuel/air mixtures; a comprehensive literature survey of explosions in unconfined vapour clouds is not attempted, since this has been the subject of numerous comprehensive reports,[1] however, a brief review of some of the background work on direct initiation of spherical detonations is included.

Some of the work described in this report was the subject of an Extra-Mural Contract with the University College of Wales, Aberystwyth, and some of the work was carried out for the Thornton Research Centre of Shell (UK) Ltd.

2 BACKGROUND

In the earliest experiments on spherical detonations conducted by Laffitte,[2] Manson,[3] and Zeldovich,[4] it was clearly demonstrated that direct initiation requires the explosive release of a relatively large quantity of energy by the ignition source. The subsequent work by Freiwald and Koch[5] on the $C_2H_2/O_2/N_2$ system, and the work of Litchfield et al[6] on C_2H_4/O_2, C_3H_8/O_2 and H_2/O_2 mixtures have illustrated that the magnitude of this initiation energy is related to the induction zone thickness in the gaseous explosive mixture. This in turn depends on the nature of the gas, the fuel/oxygen stoichiometry, the amount of inert diluent in the mixture, and the initial pressure of the gases. Under the mistaken view, however, that the sole criterion governing direct initiation of spherical detonation waves was the total source energy, some of the earlier work is of limited usefulness since the precise nature of the initiation source in terms of the temporal and spatial parameters of the energy release, ie source volume and rate of energy deposition, was not recorded, and it has since been illustrated by Bach et al[7] that for the same explosive mixture at the same initial conditions ($C_2H_2 + 2O_2$ at 4000 Pa) the magnitude of the critical ignition energy required for direct initiation differed by several orders of mignitude if different types of ignition source were used. Electrical

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sparks, laser sparks, exploding wires and chemical explosives covered a critical initiation energy range of from 0.6 joule for a laser spark of 0.02 µs duration to 450 joules for an electric spark discharge of 60 µs duration. Litchfield et al[6] quote minimum energies for direct initiation of $3H_2 + 2O_2$ at atmospheric pressure of 82 and 12.5 joules for electric spark and exploding wire respectively. The values quoted by these authors refer to the energy stored in a capacitor bank used to initiate the discharge, and it is noted that not all this energy will be delivered to the gas, and will of course be different for the two modes of initiation.

Bach et al[7] tried to reconcile the differences between the critical initiation energies for the various types of ignition source by introducing the concept of a critical average power density, defined as (total source energy)/(maximum source volume) × (total time of energy release), with some success. The power density for the 0.6 joule laser spark and the 450 joule electric spark is the same for both cases - 3×10^{17} W/m^3. They point out, however, that the power density alone cannot be a physically meaningful parameter that can be related to the properties of the gaseous explosive. The reason is that the source energy can be made vanishingly small and the power density maintained constant through the appropriate reduction in the discharge time or the source volume. With presently available mode-locked lasers, pulses of the order of picoseconds can be achieved, and for the magnitude of the critical power density quoted above, the energy required would be of the order of microjoules.

The well-established experimental fact cited for example by Lewis and von Elbe[8] that just the ignition of a combustible mixture alone requires minimum energies of the order of a millijoule lends support to the argument that the energy required to initiate a detonation cannot be arbitrary and hence power density alone cannot be a meaningful parameter. It seems reasonable to assume that irrespective of the source used, a certain minimum energy must be deposited in such a way as to generate a blast wave in the gaseous system which is of sufficient peak pressure and positive duration to raise the temperature of the gas to a sufficiently high value for a sufficiently long time to induce the hydrodynamic and chemical kinetic conditions required for detonative reaction. One approach therefore is to attempt to define the minimum strength and duration of the required blasr wave. Experimental work of Alcock et al[9] has

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shown that the hydrodynamic flow structure of a spherical blast wave generated by a laser spark is in good agreement with point-blast theory, even at times very early after the termination of the laser pulse. This enabled Lee and his co-workers[10] to correlate experimentally measured critical laser spark initiation energies with those predicted by an idealized-point-blast theory.

Any comprehensive theory covering the initiation of spherical detonations must cover the case of the three distinct propagation mechanisms that may occur. These are as follows:

a   The Super-Critical Regime - where the initially overdriven spherical detonation decays continuously to a multi-headed detonation wave with a velocity of propagation within a few per cent of the theoretical Chapman-Jouguet (C-J) value.

b   The Sub-Critical Regime - where the mixture is capable of detonation, but the initiation energy is below that required for direct initiation. In this case the overdriven shock wave decays rapidly, and the reaction zone decouples from the shock front, with the result that the wave ultimately decays to a spherical deflagration wave.

c   The Critical Regime - when the initiation energy is a certain critical value, the initially overdriven wave at first decays, and decoupling of the shock front and the reaction zone occurs. However, unlike the sub-critical regime, where decoupling progresses in an exponential manner, in the critical regime the decoupling stops when the reaction zone is a certain distance behind the shock front. The shock front and the reaction zone then propagate as a quasi-steady complex for some distance at a velocity well below the theoretical C-J value. Eventually instabilities give rise to "local explosions" at isolated spots in the spherical reaction zone, which gives rise to a wave motion which eventually achieves the C-J velocity.

These three regimes have been illustrated by Struck,[11] for C_2H_2/O_2 and $C_2H_2/O_2/N_2$ mixtures at sub-atmospheric initial pressures; typical velocity profiles as a function of time from the moment of initiation are given in Fig 1a. Brossard et al[12] have shown the initiation of spherical detonations in $C_2H_2/O_2/N_2$ mixtures for various degrees of nitrogen dilution, Fig 1b. The super-critical and critical regimes are shown. Fig 1c shows a typical result

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for the critical case as observed by Lee and his co-workers for the oxyacetylene system.

In essence the theoretical model of Lee and his co-workers considers the propagation of a point blast wave in a reacting gas, where the chemical energy released in the shock wave is a function of the local shock strength and the shock radius. In other words the effective chemical energy release per unit mass Q_e is given by

$$Q_e = Q \cdot F(M_s, Z)$$

where Q is the chemical energy release per unit mass of explosive gas and $F(M_s, Z)$ is a specified function of the shock wave Mach number, M_s, and the shock radius Z, where $Z = R_s/R_o$; R_s being the shock radius, and R_o is the characteristic explosion length, proportional to the cube root of the energy of the point initiator E_o. The function $F(M_s, Z)$ incorporates an induction distance ε during which $Q_e = 0$, and also postulates no chemical energy release below the Mach number (M_c) corresponding to that for auto-ignition. $F(M_s, Z)$ = 1 for large values of Z where $M_s = M_{CJ}$, and also for $M_s > M_{CJ}$ in the initially overdriven shock wave. In the region $M_{CJ} > M_s > M_c$ the functional form of $F(M_s, Z)$ is the lowest order polynomid that fits the boundary conditions and also gives a continuous derivative $dF(M_s, Z)/dZ$. The induction distance ε is set to that of the experimentally observed value for planar detonations. Fig 1d shows theoretical curves for the variation of shock Mach number with shock radius for various values of $\delta = \varepsilon/R_o$, which is inversely related to E_o. The theoretical model recovers the two limiting cases, ie the super-critical energy regime where the wave decays monotonically to the C-J state for very large initiation energies, ie $\delta \ll 1$, and the sub-critical regime where the blast wave decays asymptotically to an acoustic wave for very low initiation energies, $\delta > 1$. In between there is a critical value δ_c, and for values of δ slightly less than δ_c, ie E_o of the order of or greater than E_c, the blast wave decays below the C-J value and then slowly recovers to a steady velocity close to the C-J condition. The minimum valocity reached depends on the magnitude of the ignition energy, ie δ. The solution suggests that, unless the initiation energy is large, a decay below the C-J condition always occurs, and this is in agreement with the experimental observations of Struck, Fig 1a, and Brossard, Fig 1b. The theoretical solutions indicate that in the neighbour-

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hood of the critical ignition energy (ie $\delta \approx \delta_c$), the blast wave can propagate for quite some distance at a sub C-J velocity, this also accords well with the experimental observations of Lee et al,[7] who observed a sub C-J phase of almost constant velocity for 10 - 15 μs in a stoichiometric C_2H_2/O_2 mixture at an initial pressure of 13 300 Pa before instability finally accelerated the front due to the growth of explosion centres, Fig 1c.

It was also noted in the theoretical solutions that in the neighbourhood of the critical value of δ the solution exhibited slight oscillations, indicating that the coupling between the chemical reaction and the shock motion is extremely sensitive to small perturbations in this critical regime.

Following the theoretical model proposed by Lee and his co-workers, Edwards et al[13] proposed a model which related the positive duration of the initiating blast wave from a solid explosive charge to the distance between the frontal shock and the sonic or C-J plane in a self-sustaining detonation wave in the gas mixture under investigation, which is in turn derived from the three-dimensional structure of the wave. The cases of $C_3H_8/O_2/N_2$ and $C_2H_2/O_2/N_2$ mixtures are considered, and the initiation energy limits for various degrees of nitrogen dilution are compared with values predicted from the admittedly somewhat sparse data available on the detonation wave structure in these mixtures. The calculated values of charge weight necessary to initiate a given mixture agreed reasonably well with the experimental values. The mainstay of this theory was the experimental work of Vasiliev et al[14] who have shown that a sonic surface does exist in multi-headed detonation waves in tubes and that it is located at a distance well behind the region where the bulk of the chemical energy release takes place. Indeed these authors show that the sonic plane occurs at a distance of some 3 - 10 characteristic "cell" lengths behind the wavefront, when the cell length is in turn an order of magnitude greater than the "hydrodynamic thickness" of a multi-headed detonation wave. Since the hydrodynamic thickness of a multi-headed wave is considerably greater than the reaction zone width, it follows that the location of the sonic plane in a multi-headed wave is well removed from its interpretation in a one-dimensional model. However, it has been shown experimentally from pressure records that the burned gas emerging from the front of a multi-headed wave continues to be processed downstream by the "tails" of the transverse shock waves and it is only when the energy of the waves is almost wholly attenuated that the flow becomes fully

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sonic with respect to the front (Edwards et al[15]) giving considerable credibility to the work of Vasiliev.

Recent experimental and theoretical work by Lee and his co-workers[16,17] has proceeded along similar lines to Edwards et al.[13] Two parameters of the initiation source are found to be important in the case of direct spark-initiation of detonation; the peak power of the source and the energy release of the source up to the time when the peak power is achieved. The minimum power requirement indicates that the shock wave must be capable of generating a shock wave of a certain minimum strength, corresponding to about the auto-ignition limit for the explosive mixture. The minimum energy requirement, on the other hand, guarantees that the shock wave radius must exceed a certain value when the shock Mach number is that associated with the auto-ignition limit. This minimum value of shock radius is necessary for sufficient chemical energy to be released by the gas within the shocked volume so that the shock can be sustained by it subsequently.

Lee et al[18] thus proposed the concept of a "detonation kernel", and noted the close analogy between the initiation of a flame and a detonation. In flame ignition the energy source generates a volume of hot gas whose size when the temperature of the gas is of the order of the normal flame temperature should be a certain minimum size. If the size of the so-called "flame kernel" is too small, the rate of heat liberation, via chemical reactions inside the kernel, is insufficient to compensate for the rate of heat loss by conduction to the surrounding gases. In that case the temperature drops throughout the flame kernel and the reactions gradually cease. In the case of detonative initiation the source must be capable of generating a blast wave of sufficient strength to raise a given volume of gas to a temperature above the auto-ignition limit for a sufficient duration as indicated above. The radius R* of the detonation kernel is derived from shock tube kinetic data, ie

$$
R^* = \frac{M_s^* \, C_o \, \tau_{Ms}^*}{1 - \left[\tfrac{1}{2} \left(\frac{M_s^*}{M_{CJ}} \right)^2 \right]^{1/3}}
$$

where M_{CJ} is the mach number of the C-J wave and C_o is the sound speed of the unshocked gas. Of course the evaluation of the induction period τ^*_{Ms} requires

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a complete knowledge of the shock-hydrodynamic flow structure for $R_s < R_s^*$, since the molecules reacting at $R_s = R_s^*$ actually crossed the shock earlier in time, when $M_s > M_s^*$. Lee et al relate the characteristic cell size of the gaseous detonation wave to the detonation kernel size, and show reasonable agreement with experiment for oxyhydrogen and oxyacetylene systems at sub-atmospheric pressures.

These authors also note the importance of careful specification of the initiation source, be it electrical or explosive, if comparisons of experimental data on critical energies are to be made among different investigations.

In the present study pressed pellets of tetryl, initiated by exploding bridgewire (EBW) detonators, were chosen as the source of ignition for fuel/air and fuel/oxygen/nitrogen mixtures at an initial pressure of one atmosphere. Unlike the electric spark, laser spark or exploding wire techniques the power density of a detonating condensed phase explosive is not readily capable of direct monitoring. The total energy can, of course, be either calculated or measured in a bomb calorimeter, and information is available on the strength and hydrodynamic structure of the spherical blast wave generated in air by the explosive as a function of radial distance from the charge. The values of initiation energies readily available from explosive charges, ranging from hundreds of joules to megajoules, span the values necessary for the initiation of a large number of hydrocarbon/air mixtures. Also the physical and chemical form of pressed tetryl pellets can be closely specified, enabling a high degree of reproducibility in experimental results to be achieved. Consequently the experimental results obtained in the present investigation may be tested against any existing or future theoretical model.

3   EXPERIMENTAL DETAILS

3.1   The General Layout

The gaseous mixtures under investigation were contained in polythene balloons at atmospheric pressure. The propagation of the wavefront from the initiating source through the gas was monitored by means of a microwave "Doppler" radar unit which transmitted X-band microwaves (≈ 10 GHz). Some fraction of the transmitted microwave signal is reflected by the ionized reaction zone behind the shock front in the gas, and this reflected signal is combined with a sample of the transmitted signal in a microwave mixer diode. The resulting difference or "Doppler" signal thus contains a component the frequency of which is directly

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proportional to the velocity of the ionized reflecting front. This enables a continuous monitor to be obtained of the propagation of the reflecting front over the entire width of the polythene balloon. In addition a number of piezo-electric gauges monitor the blast wave external to the polythene bag. The general experimental layout is shown in Fig 2. The individual components of the system are now considered.

3.2 The Polythene Bag

The gas mixtures were contained in large polythene bags with a volume of up to 2 cubic metres and a maximum length of 3 metres. The bags were fabricated from "Layflat" polythene tubing 1.8 metres in width, 130 μm in thickness and 130 g/m^2 specific weight. The length of the bags varied from 1.80 to 3.05 metres. The bags were suspended with top edge 2.0 metres above the ground by a 30 mm diameter steel rod running the length of the top of the bag, as shown in Fig 2.

3.3 The Gas-handling System

The gas-handling system, shown in Fig 3, is capable of admitting simultaneously four gases into the polythene bag. The flow rates required to fill the bag with the test gases in the appropriate proportions were carefully calculated beforehand for each mixture composition, and the flow rates set accordingly by the needle valves and rotameters. The total volumes of the gases admitted to the bag are recorded by the integrating gas meters. Turbulent mixing of the gases occurs in a small mixing chamber prior to admission into the bag via a flame trap. A heavy-duty gate valve isolated the gas-handling equipment from the explosion and a water-filled manometer indicated the back-pressure in the gas meters. Provision was made for extraction of a sample of the gas mixture from the feed from the mixing vessel to the gas bag. This took the form of a 25 ml (previously evacuated) volumetric flask, the contents of which were submitted for gas chromatographic analysis. By virtue of the passage of the gases through water-filled gas meters, the mixture contained the saturation vapour pressure of water at the ambient temperature of the bomb chamber. This was generally $10^O \pm 2^O C$. No attempt was made to dry the gas mixtures, and all theoretical detonation parameters quoted in this report include the effect of water vapour.

The compositional accuracy of the gas mixtures was limited by the accuracy of the gas meters. Minor adjustments to the water levels in these enabled calibration of the individual meters to $\pm$ 0.25% - the figure quoted by the makers for these meters. Thus for a mixture of three gases a compositional accuracy of the order of 1% could be realised.

3.4 The Microwave Circuit

A number of variations on the microwave circuit were tried. Initially a similar system to that used by Edwards et al[19] was employed, as shown in Fig 4. The klystron is followed by a ferrite isolator and a variable attenuator. A 10 dB directional coupler samples the output power of the klystron, and is fitted with an accurately calibrated cavity wavemeter. A VSWR meter and 3-stub tuner enables mismatches in the system to be tuned out. A "hybrid" or "magic" tee directs the power from the klystron to the launching horn via the flexible waveguide; the reflected signal is monitored by the detector crystal D2. In the first instance a 30 mW Klystron type 2K25 was used; the reflected power signals were found to be inadequate to follow the entire trajectory of the detonation wave, so that it was later replaced by a 1500 mW klystron type K350 (CV5426). This klystron is a two-cavity klystron of low noise modulation and good frequency stability, oscillating at 8800 MHz. It does, however, require forced air cooling, and substantial power supplies. It is also expensive.

The pyramidal brass launching and receiving horn opened to an aperture of 146 × 118 mm and had a gain of 16 dB. The horn was fitted with a PTFE plug and a flexible waveguide coupling to give a measure of mechanical protection to the microwave circuit. It was later found that for simple "go-nogo" tests a commercial microwave doppler unit (type AEI DA 8525/6) could adequately replace the complex microwave circuit and yet give adequate performance. This device was found to be mechanically robust to the extent that it could be coupled directly to the horn without the flexible waveguide. It was also cheap.

The output of the detector diode, either from the microwave circuit or the Doppler unit, was fed through a passive high-pass filter with a cutoff at 15 KHz to an operational amplifier with a gain of 400. The doppler signal was recorded on two Datalab DL 905 transient recorders to give a data capture time of 2 milliseconds. Thus one recorder covered the period 0 - 1 millisecond sampling at 1 microsecond intervals, and the second covered the period 1 - 2 milliseconds. The output from the transient recorders was either fed on to a chart recorder,

photographed from an oscilloscope screen, or transferred to paper tape for subsequent computer processing.

3.5   The Explosive Charges

Pressed charges of tetryl were used for the explosive initiator. These were in the form of right square cylinders and had masses ranging from 2.5 to 520 grams. The charges were suspended in line with the microwave horn either at the centre of the polythene bag or at the end remote from the horn. The cylindrical charges were end initiated by an exploding bridgewire detonator fired from a 0.25 µF capacitor charged to 4 kV. The properties of the tetryl explosive used were as follows:

Energy release	4270 kJ/kg
Density	1500 kg/m^3
Gas liberated	0.845 m^3/kg
Detonation pressure	2×10^4 MPa
Detonation velocity	7.3 km/s

For some of the experiments the exploding bridgewire detonator alone was used as the initiating charge. The detonator contained 0.33 g of PETN. This was assumed to be equivalent to 0.46 g of tetryl; however the rate of energy deposition for PETN is not necessarily the same as for tetryl, and the detonator certainly produces a directional blast wave, so that there is no strict comparability that can be established.

3.6   The Pressure Gauges

An array of type B12 air-blast gauges was deployed above the polythene bag as shown in Fig 2. The size and geometry of the gas bag and the bomb chamber did not permit the ideal layout of the gauges to give the desired uninterrupted pressure record; the major problem being the close proximity of the bomb chamber walls. The array used was intended to be a compromise between these limitations. The output of the gauges was fed directly to a Tektronix 551 oscilloscope fitted with a type M plug-in.

The B12 piezoelectric gauges monitored the blast field outside the polythene bag. It was also required to monitor the shock wave pressure profiles in close proximity to the initiating charge; for instance 3 – 20 cm from a 2.5 g charge. At such close proximity to a solid explosive charge the peak stagnation pressures are such that gauges ordinarily used for blast wave

measurement, in which the sensing element is a piezoelectric crystal, cannot be used. It was decided therefore to develop a Hopkinson pressure gauge for this purpose. For the preliminary studies a silver steel bar 8 mm in diameter and 200 mm in length was used. The bar was mounted in Teflon collars located inside a stainless steel tube. A matched pair of semiconductor strain gauges, cemented diametrically opposite each other and connected in series, respond to longitudinal strains whilst those arising from flexure of the bar are cancelled. In this way a record that is remarkably free from flexural oscillations is obtained. The development of this gauge will be discussed in a future report.

A further pressure transducer was used to detect the arrival of the blast wave at the end of the polythene bag. This took the form of a small piezoelectric disc, the output of which was displayed on a Tektronix 551 oscilloscope. This was basically a diagnostic aid to determine the total propagation time of the wavefront from the initiating charge to the end of the polythene bag, and no pressure/time profiles were interpreted.

4   EXPERIMENTAL RESULTS

The description of the experimental results is divided into two main sections. As indicated in the introduction the aims of the investigation were twofold, namely to study the mechanism of initiation of spherical detonations, and to assess the sensitiveness of a number of hydrocarbon/air mixtures to direct detonative initiation. Thus this results section deals firstly with the interpretation of the microwave interferograms of the initiation process, and secondly with the experiments aimed at determining the critical initiation conditions of various fuel/air mixtures.

4.1   Microwave Signals

In Fig 5 is a sketch of the principal features of the records which are obtained of the reflected microwave power from a spherical detonation. Initially the blast wave formed by the tetryl pellet is very intense, and the reflection of the microwaves is near metallic. As the radius of the blast wave grows, so does the reflecting area, hence the signal amplitude increases as indicated by the region labelled AB. The velocity of the blast wave at this stage can be related to the slope of the voltage-time graph dV/dt by $M_s = k/R_s \cdot dV/dt$ where k is a constant which can be determined from the total reflection of the microwave power at the distance of the initiating source

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from the horn. The expanding cloud of gaseous products of detonation of the tetryl pellet will also reflect microwaves; the signal from this source will follow the same general trend as that from the ionization associated with the blast wave. The combination of these two effects is to superimpose upon the genuine doppler signal, which is of sinusoidal form in the frequency range 50 - 200 kHz, a large amplitude low frequency component AB as shown in Fig 5. If there was no loss in reflectivity of the front as the blast wave propagated out from the tetryl pellet the amplitude of the signal would continue to grow beyond B, until the total power emitted by the horn would be reflected. However as the Mach number decays below the Chapman-Jouguet value a rapid fall in frontal ionization occurs, with a consequent fall in reflected microwave power; this accounts for the observed decay in signal BC. Eventually a near steady state is attained in which the front velocity is constant and the interferogram is a regular near-sinusoidal oscillation. The values of time t and distance R given in Fig 5 are an order of magnitude indication for a 2.5 g tetryl charge in a detonating $C_3H_8/O_2/N_2$ mixture, and are not precise values for any particular mixture composition. Likewise the M_s - R plot in Fig 5 is schematic.

The precise form of the microwave interferogram was highly dependent upon the distance of the initiating source from the microwave horn, the initiating charge weight, the gas under investigation and the stoichiometry of the fuel/ air mixture. Thus with a small volume of gas and the microwave horn close to the initiating charge in a propane/oxygen mixture with little nitrogen dilution, the total velocity trajectory of the blast wave could be clearly resolved, whereas in the case of methane/oxygen mixtures with substantial nitrogen dilution, the blast wave trajectory could not be resolved in the sub-Chapman-Jouguet phase on account of the low level of ionization that obtained in that region.

Thus although in principle the microwave interferometer could be used to observe both the initiation process and the stable propagation of spherical detonation waves in a single experiment, in practice the two phenomena were investigated separately.

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4.2   The Initiating Blast Wave

The microwave interferometer has been used to follow the motion of blast waves from small tetryl pellets in mixtures of $C_3H_8 + 5O_2 + ZN_2$. For these experiments a commercial grade "Calor" propane was used. For radial distances of less than 5 cm or so from the tetryl pellet the cross-sectional area of the reflecting surface was small in relation to the microwave horn field, and thus there was some ambiguity as to the space origin on the microwave interferogram. In order to identify the space origin on the record an ionization probe was situated 5 cm from the tetryl pellet; the signal from this probe enabled the position of the blast wave corresponding to a particular instant of time to be found. Fig 6 shows a record obtained with a 2.5 g pellet initiating a detonation in $C_3H_8 + 5O_2 + 4N_2$; the upper trace showing the output from the microwave interferometer and the lower trace showing the marker pulse from the ionization probe. An analysis of this particular record is also given in Fig 6. It can be seen that at $R_s \approx 4 - 5$ cm or $t \approx 10 - 15$ µs a change of slope occurs in the graph which marks the transition from the initiating blast wave to the detonation wave. This corresponds to the minimum in the velocity-distance sketch of Fig 5. Confirmation that the velocity trajectory of the initial phase of the blast wave is being correctly monitored by the microwave system was obtained from streak shadow photographs obtained with a Beckman and Whitley 339 streak camera. Data obtained from one such record is included in Fig 6 for comparison with the microwave values. The agreement in the initial slopes of the two graphs is very close, and the slight discrepancy that occurs at their origin is no more than the experimental error. It should of course be noted that the streak camera observes the motion of the shock front whereas the microwave interferometer responds to the ionization associated with the reaction zone.

The initial trajectory of the shock wave can be represented by the relation

$$R_s \approx 13.5t^{0.9}$$

where R_s is in cm and t in µs. Lee et al[20] show that when the shock trajectory can be expressed as a power law of the form $R_s = At^N$ then the energy-time curve of an expanding piston which is supporting the shock is of the form $E = Bt^{\alpha}$ where

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$$N = \frac{\alpha + 2}{j + 3} \;,\; A = \left[\left(\frac{j + 3}{\alpha + 2} \right)^2 \left(\frac{Ba_o^2}{\gamma k_j \rho_o I} \right) \right]^{\frac{1}{j + 3}}$$

where I is an integral the numerical value of which is given by Dabora.[21]
Substituting in the above expression with $j = 2$ and $k_j = 4\pi$ we find that

$$E = 28.2 t^{2.48}$$

where E is expressed in joules and t in μs.

If it is assumed that all the chemical energy of the source, which for 2.5 g of tetryl is about 10^4 J, is available as piston energy then on this model the piston would expand for about 10 μs before all the source energy is expended. At this time the blast wave radius is $\approx 4 - 5$ cm.

It is interesting to note that the time dependence of the energy deposition by a solid explosive is similar to that found by Lee et al[20] in their pulse discharges. For example, in one case, with cylindrical geometry, they find that E (J/cm) $\approx 367 \, t^{2.26}$. Figs 7 and 8 show the variation of velocity of the shock front with radial distance for various mixtures of $C_3H_8 + 5O_2 + ZN_2$. Fig 7 shows the velocity profile from an initiating source of 2.5 g tetryl in a mixture that is easily detonable, whereas Fig 8 shows profiles from the same initiating source in mixtures that are close to the limit of detonability for that particular charge weight. Several features emerge from these records. Firstly all the records show the general features illustrated in the sketch of Fig 5, predicted by the model of Lee et al (1971) and shown experimentally by Brossard, Lee and Struck (Fig 1); that is to say a rapid decay in blast wavefront velocity from the initiating charge to a value substantially below the Chapman-Jouguet value, followed by a slow rise to a velocity that is within a few per cent of the theoretical Chapman-Jouguet value. In every case the recovery from the sub Chapman-Jouguet condition takes the form of irregular fluctuations in frontal velocity, the extent of this irregularity increasing as the limit of detonability of the mixture is approached. For mixtures well removed from the limit of detonability, ie $C_3H_8 + 5O_2 + 6.9N_2$ the Chapman-Jouguet condition is achieved at some 25 cm from the initiating source, whereas for a mixture on the limit of detonability, ie $C_3H_8 + 5O_2 + 10.2N_2$, a stable

frontal velocity is achieved at approximately twice this distance. In some
dilute systems, ie C_2H_6/Air, with larger initiating weights ($\approx$ 150 g) the sub-
Chapman-Jouguet phase is observed to propagate for distances of greater than
1 metre. In such cases velocity fluctuations were difficult to resolve clearly
owing to the low level of ionization that obtained in those waves; however
there is little doubt that such fluctuations occur in all marginal systems.
The experimental records of Struck, Fig 1a indicate this irregularity in the
sub C-J phase. It is interesting to surmise that the mechanism of decay in
wave strength and subsequent acceleration in these velocity fluctuations may
be the same as that observed in tubes, that is "cyclic" or "galloping"
detonations. This phenomenon was observed by Mooradian et al[22] and studied in
mare detail by Saint-Cloud et al[23] and Edwards et al.[24] Galloping detonations
in tubes exhibit a regular fluctuation about the Chapman-Jouguet velocity,
where the wavelength of these fluctuations is typically 2 - 4 metres. The
scale of the unconfined detonations described in this report is not sufficiently
large to establish whether in the spherically divergent situation the velocity
fluctuations would propagate indefinitely, or whether the wave would ultimately
either achieve the Chapman-Jouguet state or decay to a sonic wave. In any
case the phenomenon of galloping detonations occurs only over a very narrow
range of compositions near the limit of detonability of the mixture, and was
not the subject of the present investigation.

4.3 The "GO-NOGO" Test

One of the principal aims of the present investigation was to study the
limits of detonability of fuel/air and fuel/oxygen/nitrogen systems. This is
an area which has received scant attention in the literature in the past,
probably since it is generally true that, in the case of hydrocarbon/air
systems, substantial initiating charges and volumes of gas are necessary.
Ideally a very large volume of gas would be used to establish unequivocally the
limit of detonability of the mixture. In practice this is not generally
possible. Thus in the present series of experiments considerable attention was
given to the problem of using the minimum volume of gas consistent with
achieving reliable and unambiguous results.

Distinction between experiments in which detonation occurred and those in
which the wave failed was usually simple and unequivocal by reference to the
nature of the microwave interferogram. For "go-nogo" tests the initial stages
of the wave propagation were not recorded, as these were essentially the same
in either case of a "go" or a "nogo". Fig 9a and b show typical microwave
interferograms for the case of a "go" and a "nogo" respectively. In region AB
of Fig 9a an oscillating signal of steady frequency denotes a reflective wave
moving at a constant velocity calculable from its frequency and the free-space
wavelength of the microwaves. In such a record the velocity invariably turns
out to be within a few per cent of the theoretical Chapman-Jouguet values for
the particular gas mixture. At B the polythene bag is ruptured and thereafter
the interpretation of the record becomes problematical. In Fig 9b the initia-
ting charge weight is such that detonation is not induced in the gas mixture.
In this case there is a complete absence of regular sinusoidal fluctuations.
The record is terminated by the rupture of the polythene bag. In Fig 9c the
initiating charge weight is near the limiting value for initiation of detona-
tion. In this case there is some evidence of a sinusoidal fluctuation at a
frequency consistent with a wave travelling at the Chapman-Jouguet velocity,
albeit with reduced amplitude and limited duration, as shown in region CD.
In such cases the amplitude of the sinusoidal oscillations may be comparable
in amplitude to the background noise, and it may be necessary to Fourier
analyse sections of the record to determine the strength and frequency of
such fluctuations. There is thus a certain degree of ambiguity in the
records from mixtures on the limit of detonability; however the criterion
that was adopted was that if a sufficient number of sinusoidal oscillations
were present to enable a wave velocity close to the Chapman-Jouguet value to
be identified, then, had a sufficient path length been available, a stable
detonation would have been observed. Some justification for this criterion
was obtained from the fact that mixtures that appeared to be highly marginal
in polythene bags of 1.8 metres in length generally indicated a clear detona-
tion in bags 3 metres in length. However the microwave interferogram formed
only one of a number of pieces of evidence as to whether a detonation
propagates in the mixture, as will be discussed later. The choice of bag size
in each experiment was so as to arrange that the ratio (per unit steradian) of
the energy of the initiating charge to the total energy within the system was
always less than 1% by the time that the wave had arrived at the far end of

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the bag; in most of the experiments it was less than 0.5%, thus when the initiator charge was increased, larger bags were used.

A preliminary experiment was conducted with 20 g charges of tetryl to establish whether the position of the initiator had any effect on the measured value of the critical nitrogen concentration in a Fuel/oxygen/nitrogen mixture. The mixture chosen was $CH_4 + 2O_2 + ZN_2$. Two sets of tests were carried out, one with the initiator charge suspended at the centre of 3.05 m × 1.52 m bags, the other with the charge at the end of 1.8 × 1.8 m bags. The results are presented in Fig 10, from which it can be seen that there was essentially no difference in the propagation limits in those tests in which the sample of gas was detonated at one end and those in which it was detonated centrally. Moreover the initial velocity profile was independent of the siting of the initiator. This is a useful result, because it allows a spherically propagating detonation wave to be followed over a much greater radial distance for a given total volume of gas, and hence for a given liberated explosive power. The lack of a sufficient radial path length for observation of the wave has hitherto been one of the major obstacles to experimental progress in the study of spherically propagating detonation waves. The result of course only applies to the particular bag geometry and thickness used in the present investigation, and caution should be exercised in generalising this result.

It will be noted in Fig 10 that two of the experimental points near the propagation limit are neither clear detonations nor clear deflagrations. For this mixture and initiating charge weight, $CH_4 + 2O_2 + 3.75N_2$ and 20 g of tetryl, there exists a "grey" area where it is difficult to assess with confidence whether or not the mixture has detonated. This region of uncertainty becomes wider for more dilute mixtures and larger initiating charges. Recourse has to be made in such cases to diagnostic evidence other than the microwave interferometer.

(a) In common with all encased explosive systems, a measure of the violence of the event can be gained from the fragments of the polythene bag that are recovered. In the event of a detonation, the fragments of the bag were small, with the majority of the pieces less than 50 mm in diameter, and the remainder typically less than 150 mm in diameter. For the case of a deflagration, there are few small fragments, and large sections of the bag may be recovered intact. Few fragments will be less than 150 mm in diameter.

(b)   The peak pressure of the blast wave outside the bag will be less in the case of a deflagration than in the case of a detonation. This will be shown by the records from the array of piezoelectric B12 blast gauges mounted vertically above the bag.

(c)   The arrival time of the wavefront at the end of the bag remote from the initiating charge will be greater for a deflagration than for a detonation. This will be witnessed both on the microwave interferogram (point B in Fig 9a) and on the piezoelectric "marker" affixed to the end of the bag.

These additional diagnostic techniques are of considerable assistance in limit determining experiments which use a successive approximation technique. The numerical values for limits quotes in this report, however, are those from completely unambiguous records. For instance experimental records where the evidence of the microwave interferometer is at variance with that of the pressure gauges (ie the points denoted + in Fig 10 are discounted from the analysis).

The techniques used to determine the limit of detonability of the various fuel - air and fuel - oxygen - nitrogen system varied slightly for the different gases; these are now considered in turn.

1   Methane

It has long been recognised that it is very difficult to establish a self-sustaining detonation in the spherical mode in methane-air mixtures. In general it is more difficult to establish a detonation in the spherical mode than in a tube, and Kogarko[25] found it necessary to use tubes of very large diameter to obtain satisfactory propagation of a detonation wave in methane/air. It is therefore no surprise that until recently there have been few attempts to study spherical fuel-air detonations with methane as the fuel, although natural gas-air detonations have been reported by Vanta et al[26] (96% CH_4 - 4% higher hydrocarbons). Kogarko's experiment[27] on spherical detonations in a methane/air mixture may be criticised on the grounds that the path length available was insufficient to ensure that the behaviour of the wave was free from the effects of the solid explosive charge used as the initiator. Kogarko's experiment showed that a charge weight of 1 kg of TNT would initiate a detonation in stoichiometric CH_4/air. However, the measured detonation velocity, 1540 m/s, was well below the theoretical value, $\approx$ 1800 m/s.

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The experiments described in the present report were aimed at determining the limits of detonability of various methane/oxygen/nitrogen mixtures with varying degrees of nitrogen dilution with a view to obtaining a reliable extrapolation to the methane/air case. A stoichiometric mix was used throughout. The critical nitrogen concentration for six different masses of initiating charge was determined. The charge weights were 0.46, 2.96, 20.46, 71, 154 and 540 grams respectively. The results are shown in Fig 11. All the charges were tetryl except that of the 0.46 g charge, which is the equivalent explosive weight of an EBW detonator. For the majority of the tests the microwave interferometer and the blast gauges agreed in their diagnosis of detonation. There were however five tests in which the blast gauges indicated detonation but no clearly periodic signal was recorded by the microwave interferometer. These results are represented by the distinct symbol (+) in Fig 11, and were omitted from the statistical treatment of the results. To identify a boundary in the charge weight - nitrogen dilution plane, the highest value of nitrogen dilution which detonated and the lowest value which did not were noted for each charge weight. Then treating these results as censored observations a regression analysis was employed which assumed that $\log_{10}W$ was a linear function of nitrogen dilution Z. This analysis predicted that a charge weight of the order of 18 kg would be required to initiate a detonation in a stoichiometric mixture of methane/air, as shown in Fig 11. This figure also shows that the assumption of a $\log_{10}W/Z$ relationship is justified. Values of detonation velocity as a function of Z are given in Fig 12.

2 Propane

Two separate series of experiments were performed with propane as the test fuel.

(a) The effect of nitrogen dilution on the minimum charge weight of tetryl necessary for initiation of detonation in propane/oxygen/nitrogen mixtures was investigated for three charge weights; 0.46, 2.96 and 20.46 grams. For these experiments the principal aim was the investigation of the initial trajectory of the blast wave from the tetryl pellet initiating a spherical detonation. The gas used in these experiments was commercial grade "Calor" Propane. An analysis of this gas showed it to contain 90% C_3H_8, the remainder being a mixture of nitrogen and other hydrocarbons; however the precise composition of the gas obtained from such a cylinder depends to some extent on how full the cylinder is, and thus these results, shown in Fig 13, were used only as a guide as to the

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charge weight necessary to initiate a detonation in a mixture of pure propane/air. Detonation velocity is plotted as a function of Z for the 2.95 g charge in Fig 14. A regression analysis of the "Calor" Propane/oxygen/nitrogen results indicated a charge weight of 100 g of tetryl as being necessary to detonate a mixture of "Calor" Propane and air. Benedick et al[28] find that 150 g of sheet explosive will detonate a commercial grade (95% pure) propane in air, with a stoichiometry ratio ϕ of 1.19. These authors also find that a charge weight of 800 g of sheet explosive will detonate the same propane in air with stoichiometry ratios from 0.74 to 1.8. Kogarko[27] finds that 155 g of TNT will detonate a stoichiometric propane/air mixture; this author does not quote the purity of the fuel.

(b) In order to obtain a value for the minimum charge weight necessary to initiate a detonation in a mixture of pure propane and air, varying charge weights of tetryl were fired in a stoichiometric mixture of pure (> 99%) propane and air. These results are also shown in Fig 13. 80 g of tetryl reliably initiated the mixture, whereas 50 g did not. In the case of a 60 g charge the result was a highly marginal detonation; some 7 cycles of doppler signal were observed at a frequency characteristic of the C-J detonation velocity. In the case of a stable detonation in this mixture the measured detonation velocity was 1844 m/s, compared with the value calculated by Kogarko et al[27] of 1850 m/s. These authors obtain an experimental value of 1730 m/s. The difference between the results predicted from the "Calor" Propane/oxygen/nitrogen tests and that observed in the case of pure propane may possibly be accounted for by the difference in stoichiometry that obtained in the two mixed on account of the high level of impurity in the "Calor" Propane.

3 Acetylene

Acetylene was not investigated in the present study because the results of Freiwald and Koch[5] were obtained under similar experimental conditions, ie balloons of capacity 15 - 500 litres. These authors obtained the limit of detonability of $C_2H_2/O_2/N_2$ mixtures for various nitrogen dilutions, and for the sake of completeness their results are included (Fig 15). It will be noted that a charge weight of less than 1 g of tetryl will initiate a detonation in a mixture of $C_2H_2 + 2O_2 + 7.54N_2$, ie acetylene/air. This is of course not the stoichiometric mixture. It will be noted that in contrast

to the methane and propane results there is not a linear $\log_{10}W/Z$ dependence
at high values of Z. It is not possible to say from the evidence available
whether this is a general effect for $Z > Z_{air}$, or whether the result is
peculiar to this fuel/air mixture, or merely due to the particular variety of
charge configurations used by these authors. Kogarko et al[27] find that a
charge of 1.5 g of TNT will-initiate a stoichiometric mixture of acetylene and
air.

4   Butane

The results for a stoichiometric butane/air mixture were very similar to
those of propane/air, ie 80 g of tetryl gave a clear detonation, 50 g gave a
deflagration, and 60 g gave a marginal result – one firing showed 6 cycles of
microwave oscillation at a frequency corresponding to the C-J value, a repeat
firing gave a deflagration. Benedick et al[28] show that 800 g of sheet explosive
will initiate a butane/air mixture over a stoichiometry ratio of 0.8 to 1.7.

5   Isobutane

A stoichiometric mixture of isobutane/air proved to be marginally less
sensitive than n-butane/air. Thus a charge of 100 g was required for reliable
initiation of detonation, whereas 80 g gave a deflagration.

6   Ethylene

The minimum charge weight required to initiate a detonation in stoichio-
metric ethylene/air lies between that for acetylene and propane. Thus a charge
of 15 g of tetryl initiated a detonation whereas a charge weight of 10 g failed
so to do.

Ethylene/air mixtures gave particularly clear microwave interferograms,
enabling the trajectory of the reaction front to be followed from the initiation
source to the end of the bag. Also, for initiation energies close to the limit
of detonability, the irregular fluctuations in front velocity in the region
where the wave is recovering to the C-J value are particularly marked. A typical
record, along with its interpretation in terms of velocity-time and velocity-
distance trajectory, is shown in Fig 16. In the region AB of the microwave
interferogram the interpretation of the record is complicated by electrical
interference from the high voltage detonator; however between B and C there
is a strong signal corresponding to a velocity of about 800 m/s. Acceleration
in the region CD is indicated, but dependent upon the confidence placed on

individual cycles of doppler frequency, two alternatives represented by the curves P and Q may be suggested. The curve Q is thought to be the more realistic interpretation; extensive evidence from work using smoked foils in spherical bomb chambers, as yet unpublished, gives credence to the postulate of successive attempts by the shock and reaction zone to recouple prior to the establishment of a stable C-J wave.

7   Ethane

Two series of experiments were conducted on ethane/air mixtures.

(a) The minimum charge weight necessary to initiate a detonation in the stoichiometric mixture was assessed by using varying sizes of tetryl booster. 40 g gave a reliable detonation, whereas 30 g gave a deflagration.

(b) The effect of varying the fuel/air stoichiometry was investigated. The rich and lean limits of detonability were established for charge weights of 520, 154, 50, 40 and 20 grams. The results are shown in Fig 17, where the "go-nogo" points are plotted as a function of stoichiometry ratio ϕ. It will be noted that the curve shows a minimum for a slightly fuel-rich mixture, $\phi = 1.15$.

4.4   Pressure Records

In order to characterise the flow field of the initiating charges, the B12 blast gauges were used to record the blast of the tetryl pellets alone in air; typical results for the mid and far field are shown in Fig 18. The near field was monitored by a Hopkinson bar gauge; typical results for a 2.5 g tetryl charge are shown in Fig 19, the measurements were taken along the axis of initiation, and show some directional enhancement. In general the peak pressures and positive durations of the blast waves correlated reasonably well with values quotes by Petes.[29] Lee et al point out that it is not meaningful to specify the critical initiation conditions solely on far field measurements, as direct initiation occurs close to the source, and thus further work is in progress on development of Hopkinson bar gauges to monitor the flow field close in to explosive charges.

4.5   Gas Mixtures - Sensitisation and Inhibition

It is evident that there is a considerable difference in the sensitiveness of the various hydrocarbon-air mixtures to direct detonative initiation,

varying from less than a gram of tetryl to initiate acetylene-air to greater than 10 kilograms to initiate stoichiometric methane-air. This naturally leads to the question as to whether small quantities of a "sensitive" hydrocarbon will dramatically reduce the critical initiation energy of an "insensitive" system such as methane-air. This is particularly pertinent to the case of natural gas, which consists primarily of methane, but contains significant fractions of ethane, propane, butane, and pentane, Table 1[30] shows the constitution of natural gas from a number of sources; it is seen that ethane is the most abundant impurity in all cases. It has been shown that a stoichiometric ethane-air mixture is the most sensitive of the impurities generally found in natural gas. A series of experiments were therefore conducted with mixtures of stoichiometric methane/air and ethane/air in various proportions. The results are given in Fig 20. It was not possible to establish the minimum initiation energy for mixtures approaching 100% methane since the maximum initiating charge that could be fired in the bomb chamber was 540 g. Vanta et al[26] claimed to observe detonation in a natural gas-air mixture (Table 1) with a 1 kg charge. The evidence of their measured values of velocity of detonation (1195-1325 m/s) casts some doubt on this assertion; it is more probable that a quasi-steady sub C-J wave was observed, as is characteristic of an initiation energy near the critical value. The mixture which gave a detonation was not stoichiometric, being nearer $\phi = 0.9$.

5   DISCUSSION AND CONCLUSIONS

1   A simple microwave interferometer has proved to be capable of giving accurate information on the initial trajectory of the blast wave generated in a reactive gas mixture by a small explosive charge of tetryl.

Following the decay of this blast wave to a velocity below the Chapman-Jouguet value of the gas mixture, the initiated gaseous detonation, particularly near the limit of detonability of the composition, is found to exhibit velocity instability as it approaches the steady C-J value.

2   A steel pressure bar gauge was successfully used to record the blast wave field close to the tetryl pellet, however further work is required with smaller diameter bars to improve the frequency response of the gauge.

3   Spherical detonation of well-mixed stoichiometric mixtures with air of each of ethane, propane, n-butane, iso-butane and ethylene have been demonstrated unequivocally. Direct detonative initiation has been demonstrated

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in various stoichiometric methane/oxygen/nitrogen and propane/oxygen/nitrogen mixtures, and in ethane/air mixtures of various stoichiometries. Various stoichiometric methane/ethane/air mixtures have also shown detonative propagation.

In every case the steady state velocities have been measured with the microwave interferometer, these have accorded well with theoretical values.

4   The relative detonabilities of the various hydrocarbon-air mixtures have been quantified in terms of the weight of tetryl explosive required to give direct detonative initiation. In experiments resulting in gaseous detonation the path lengths were sufficiently long for sustained detonation to be observed unequivocally. Typically the contribution of the initiator charge energy to the total energy, per unit solid angle, released in the wave had reached less than 0.3% by the time that the wave reached the bay end wall. This was achieved in a consequence of the preliminary experiments (Fig 10) which showed that there was no essential difference in the propagation limits when the sample of gas was initiated at the end of the gas volume, and those in which central initiation was employed. This useful result allowed a spherically propagating detonation wave to be followed over a much greater radial distance for a given liberated explosive power; the lack of suffi-cient radial path length between the initiating explosive charge and the boundary of the gas volume has in the past represented an obstacle in the study of unconfined gaseous detonation waves, particularly in the "less sensitive" mixtures such as methane.

5   In making comparison between the detonability of the saturated hydro-carbons we see (a) that methane-air is likely to be very much more difficult to detonate than the next three homologues, (b) ethane-air is easier to detonate than propane and n-butane/air mixtures, whilst (c) iso-butane is slightly more difficult to detonate.

Comparison of the gasdynamic factors and the enthalpy terms do not reveal differences of sufficient significance to account for any of these findings. The high temperature oxidation rate data (arbitrarily computed for 2000 K in Table 2) does however roughly parallel the trends of (a) and (b) above. No shock tube data are available to make a comparison between n-butane and iso-butane, but auto-ignition data at rather lower temperatures imply that iso-butane has a somewhat lower oxidation rate than n-butane.

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Similarly comparison of the data on ethylene/air and acetylene/air with that of ethane/air reveals large kinetic rate differences and only slight enthalpy differences (these account almost entirely for the differences in the C-J properties). It appears again to be the difference in reaction rate which makes ethylene and acetylene significantly easier to detonate than ethane.

Correlation of the detonability data with kinetic oxidation rate is important because (a) it has been long known that the thickness of the detonation front is proportional to an induction length derivable from the chemical kinetic induction period and the gas flow relative to the leading shock, and (b) the structure of the detonation front also defines the coupling of the combustion energy to sustain the global motion of a detonation wave; as conditions tend to those just subcritical to detonation, it is this structure which widens and fails.

6   The region in which the establishment of a detonation is critically decided appears to be that zone in which the decaying reactive blast wave, of strength below the C-J value, undergoes a re-acceleration process; this is shown in Figs 1a, 1b, 1c, 7, 8 and 16. Our microwave doppler module does not monitor the shock front position, so that it is not at present possible fully to describe the nature of this critical region, however, recent work using the smoked foil technique, as yet unpublished, does seem to indicate that the region of re-establishment in a critically initiated spherical detonation bears a striking resemblance to flame-to-detonation transitions observed in tubes. There is also a marked similarity to the re-establishment phase of galloping detonations. Further work with schlieren photography will be necessary to fully elucidate this mechanism.

7   The minimum initiation energy of one hydrocarbon, ethane, has been established as a function of stoichiometry; it is noted that the limits of detonability lie within the flammability limits, and that the minimum initiative energy condition lies on the fuel-rich side of the stoichiometric condition, $\phi = 1.15$. This is close to the minimum flame ignition energy stoichiometry measured by Moorhouse et al[30] using an expanding capacitor plate technique ($\phi = 1.17$). It would also appear that the lean and rich limits of detonability are not far removed from the ignition limits quoted by these authors. There are, of course, many orders of magnitude difference in the energy required for flame ignition and that required for direct detona-

tive initiation, however the above result would be very useful if it could be applied to all fuel/air systems.

8   The results for stoichiometric mixtures of methane/air and ethane/air tend to indicate that the more sensitive component has an enhancing effect on the detonability of the mixture, but that this effect is not very marked. The enhancement may be due in part to the fact that ethane/air is more sensitive in fuel-rich ($\phi = 1.15$) mixtures, whereas all the evidence points to methane/air being more sensitive to fuel-lean mixtures ($\phi = 0.9$), so that a mixture of the two stoichiometric systems might appear more sensitive on these grounds alone. In order to quantify this, it would be required to establish the initiation energy-stoichiometry curve for methane-air, an extremely laborious process since it would be necessary for each stoichiometry to use varying degrees of nitrogen dilution in the methane/oxygen system to extrapolate to the air case.

6   SUGGESTIONS FOR FURTHER WORK

1   A thorough experimental investigation of the minimum initiation energy of all the volatile hydrocarbons as a function of stoichiometry would be usedul in assessing the likely affects on the environment of the detonation of a cloud of such a material following an accidental spillage.

2   Combined schlieren photography and microwave interferometry of the initiation phase of a spherical detonation would contribute to the understanding of this phenomenon.

3   At present solid explosive charges represent the only initiator method capable of spanning the range of source energies required. They do, however, add certain unattractive complexities to the gasdynamics, due to such effects as directional blast, "jetting", and failure to "scale" for small charge sizes. A thorough characterisation of the near field air blast from various charge sizes, using a Hopkinson bar gauge, would clarify the situation..

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TABLE 1

Properties of Natural Gases*

	Composition Volume %			
	Dutch	Sahara**	North Sea	US Natural Gas***
CH_4	81.76	86.5	91.8	96.05
C_2H_6	2.73	9.42	3.5	2.47
C_3H_8	0.38	2.63	0.8	0.032
C_4H_{10}	0.13	1.06	0.3	0.14
Pentanes and higher	0.16	0.09	0.33	0.04
CO_2	0.87	-	0.43	0.074
N_2	13.96	0.3	2.8	0.024
He	0.01	-	0.04	-

*Reference 31

**as distributed from the Canvey terminal

***as used by Vanta et al (Ref 26)

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TABLE 2

Detonation Properties of Stoichiometric Fuel/Air Mixtures

	Gases in Stoichiometric Mix with Air	Methane	Ethane	Propane	n-Butane	iso-Butane	Ethylene	Acetylene
Enthalpy terms	Heat of combustion of fuel/air mix (at 298K) MJ m^{-3}	3.62	3.77	3.81	3.84	3.83	3.94	3.96
Theoretical (C-J) values+	Detonation pressure ($\times 10^8$ Pa)	17.93	18.75	19.04	19.22	19.17	19.16	19.97
	Detonation temperature, K	2756	2791	2799	2802	2798	2902	3387
	Specific heat ratio, γ (at detonation temperature)	1.170	1.168	1.167	1.164	1.166	1.162	1.157
	Detonation velocity, m s^{-1}	1800	1800	1797	1795	1794	1822	1863
Experimental results	Detonation velocity, m s^{-1} (Microwave doppler measurement)	-	1760	1800	1829	1793	1780	1870**
	Tetryl initiator charge weight, kg (a) (b)	18* —	0.04 0.03	0.08 0.05	0.08 0.05	0.10 0.08	0.015 0.010	0.0015 -**
Shock Tube kinetic data $\oint$	Pre-exponential factor $\beta \times 10^{10}$ s	1.081	1.556	0.353	0.286	-	24.37	-
	Activation energy E kJ mole^{-1}	194.6	144.0	176.6	176.6	-	74.9	72.4
	Induction period τ μs at 2000 K $\{\tau = \beta e^{E/RT}\}$	13.0	0.89	1.44	1.17	-	0.22	0.27

+ Calculated for water-saturated gases at initial temperature of 283 K assuming equilibrium kinetics

* Extrapolated Value

** TNT results of Kogarko

(a) To cause gas detonation

(b) Insufficient to cause gas detonation

$\oint$(1) Methane - Butane from Burcat, Scheller & Lifshitz ((1971) Comb & Flame 16, 29)

(11) Ethylene from White ((1966) 11th Symp Int Comb, 147)
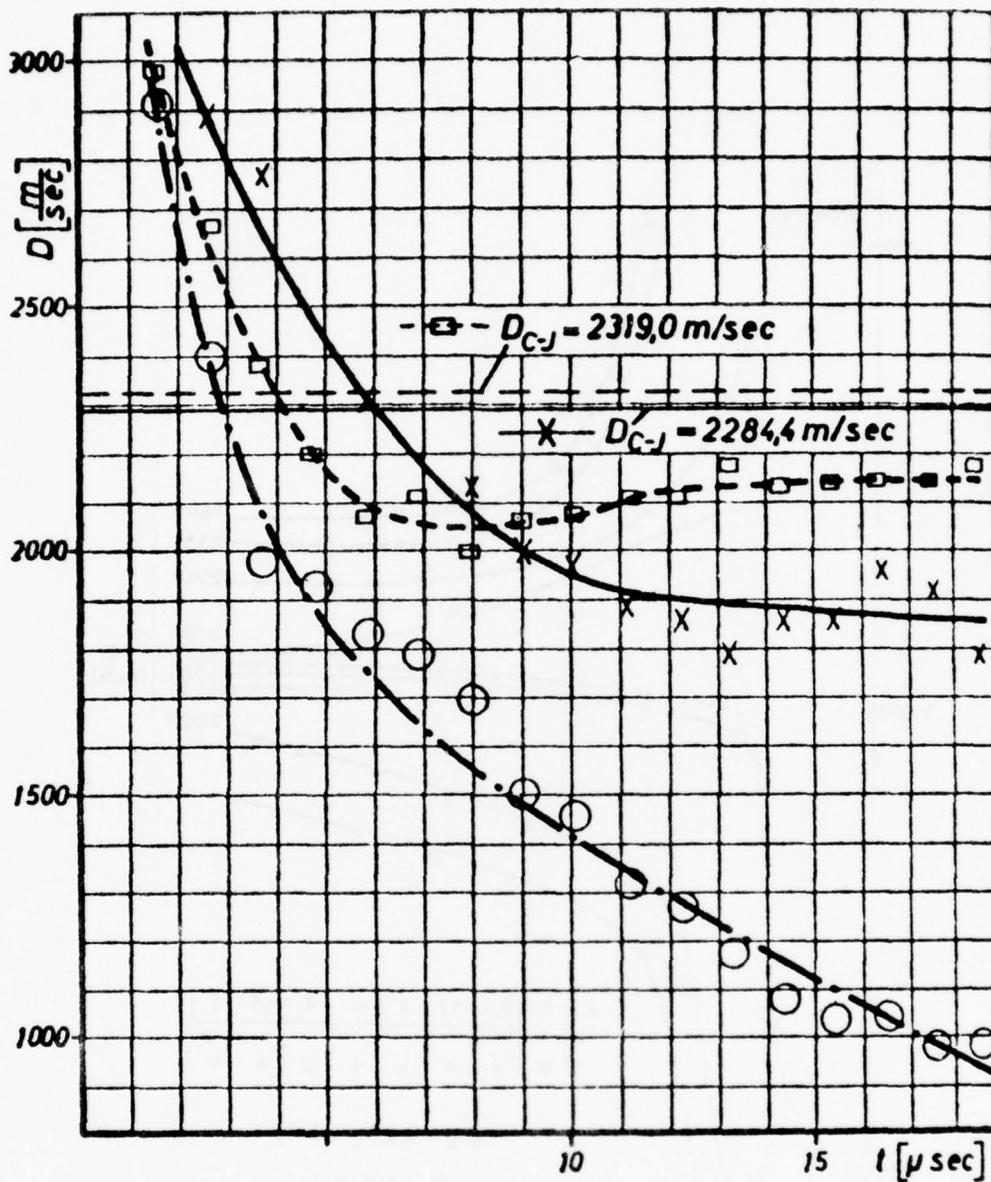
FIG. 1a VELOCITY–TIME PROFILES OBTAINED BY STRUCK[11]

----□ STOICHIOMETRIC OXYACETYLENE, INITIAL PRESSURE 13·3 kPa

——— x STOICHIOMETRIC OXYACETYLENE, INITIAL PRESSURE 6·6 kPa

—·—·—O STOICHIOMETRIC OXYACETYLENE, WITH THE ADDITION OF
19% NITROGEN, INITIAL PRESSURE 16·2 kPa
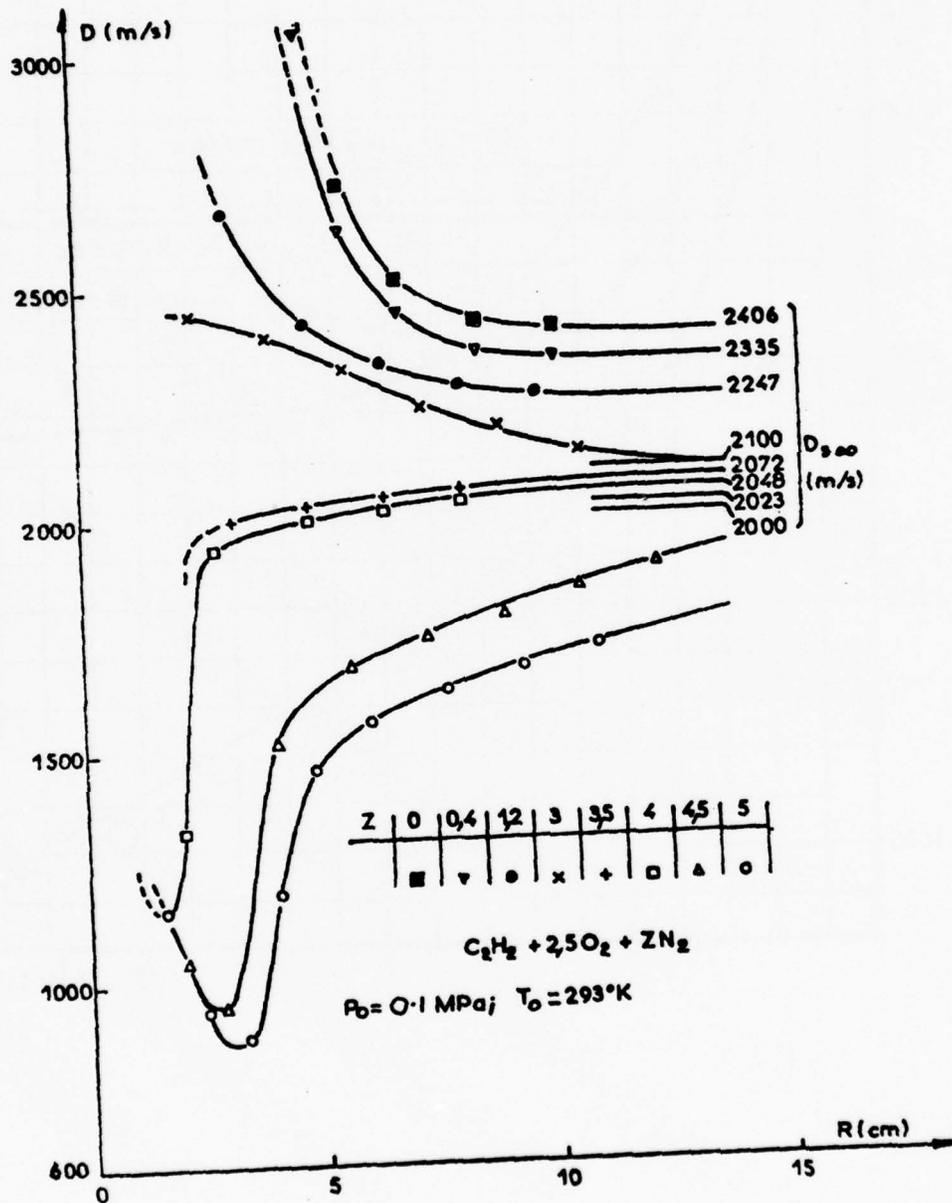
FIG.1b VELOCITY—DISTANCE PROFILES OBTAINED BY BROSSARD[12]
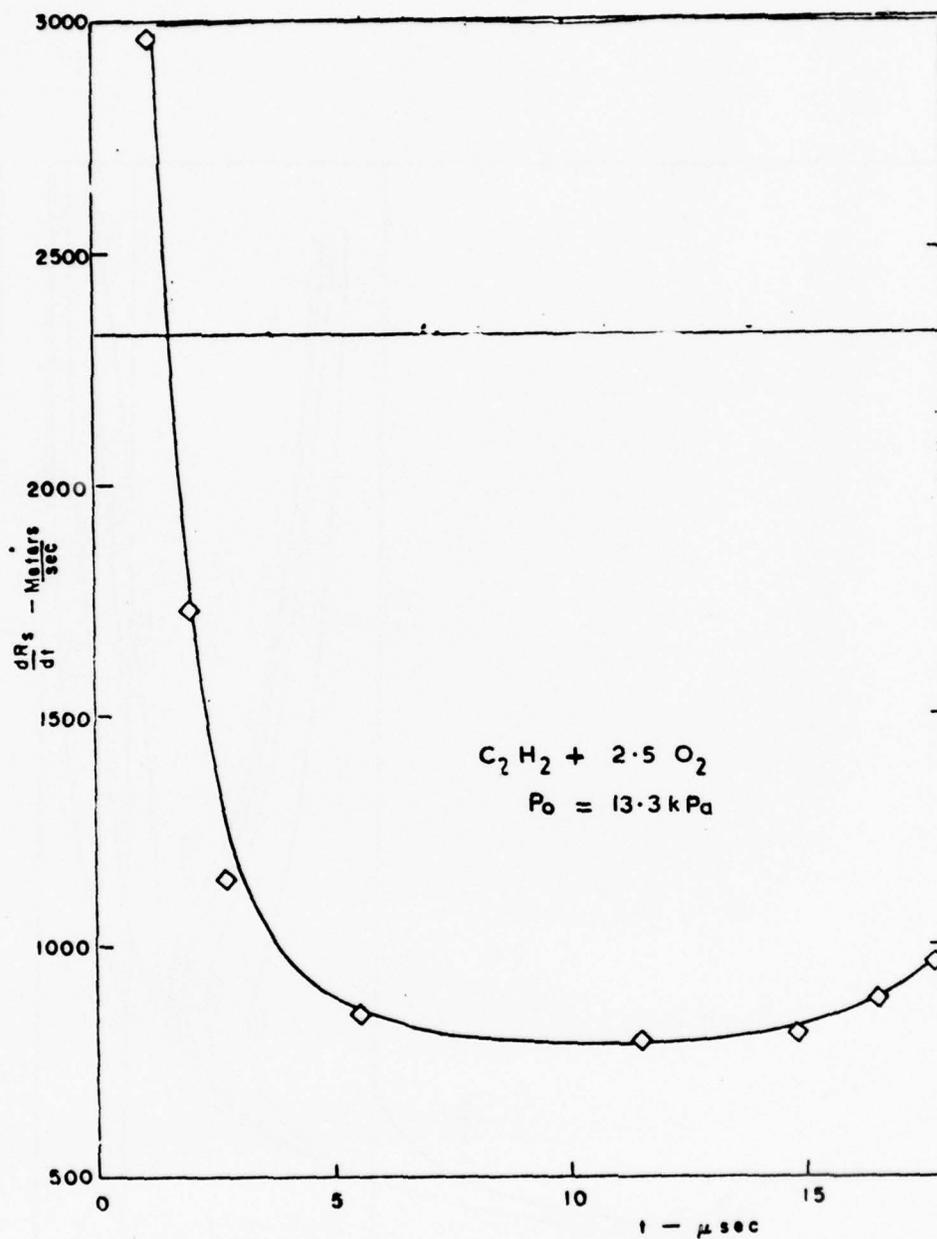
FIG. 1c VELOCITY-TIME PROFILES OBTAINED BY LEE[10]
STOICHIOMETRIC OXYACETYLENE, INITIAL PRESSURE 13·3 kPa
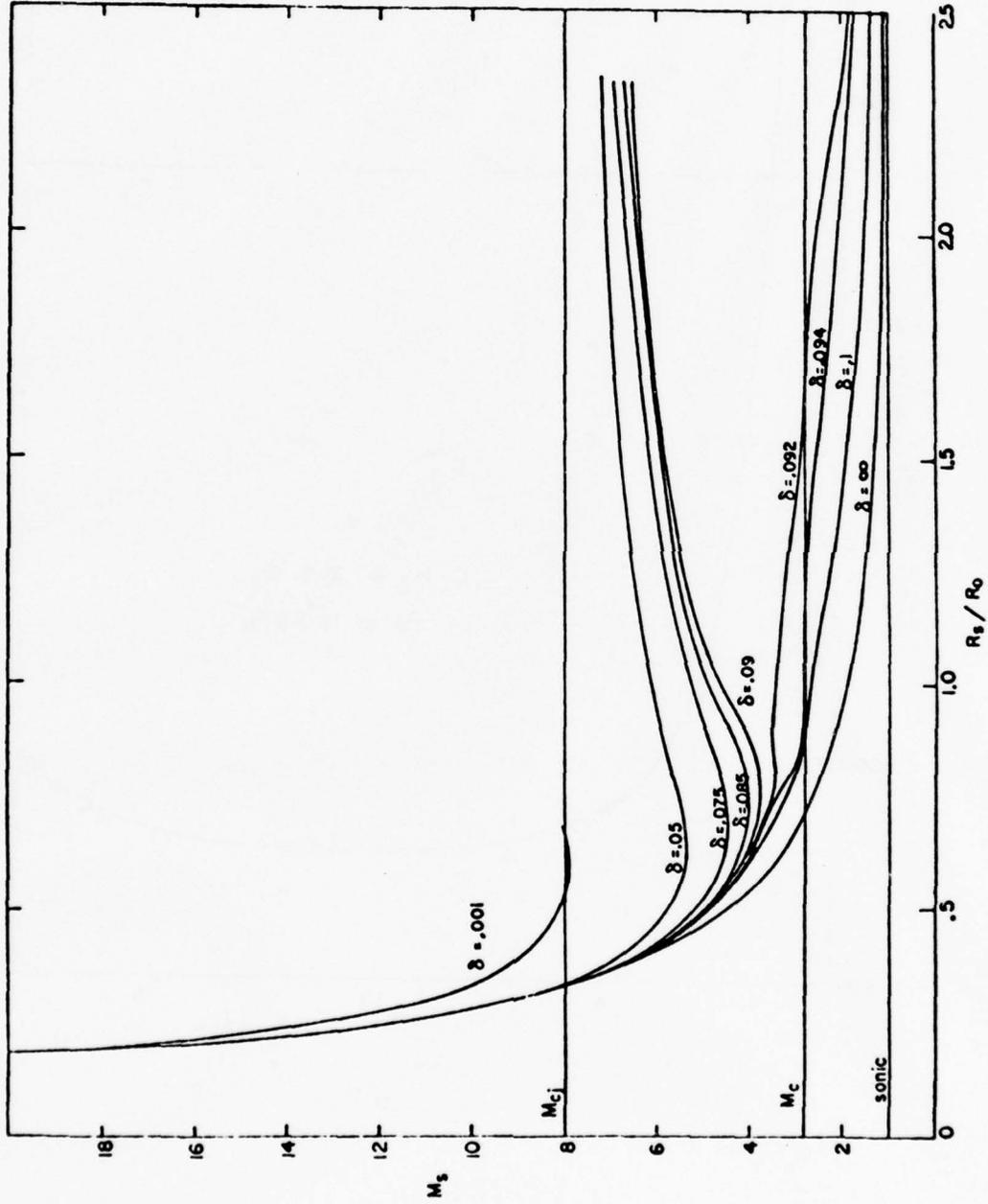
FIG. 1d THEORETICAL VELOCITY–DISTANCE PROFILES OBTAINED BY LEE[10]
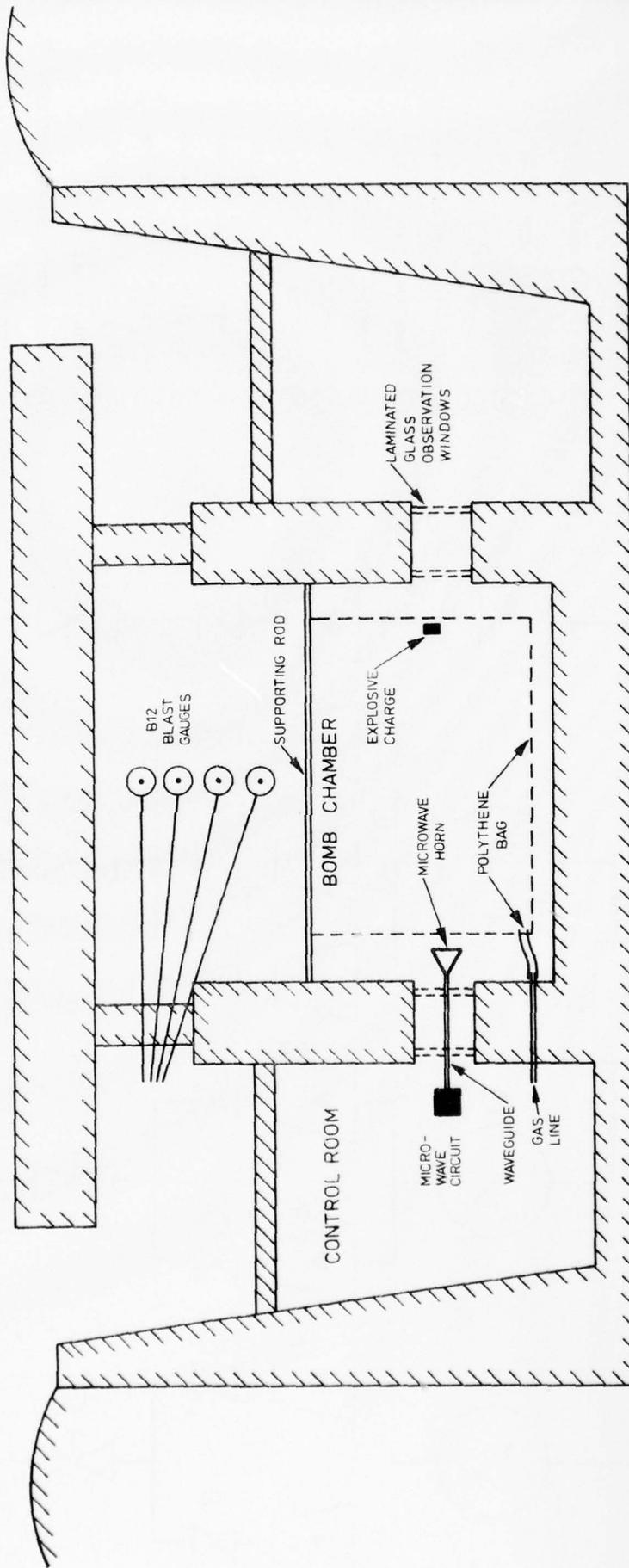
FIG. 2 EXPERIMENTAL SET-UP IN THE BOMB CHAMBER

FIG. 3 THE GAS HANDLING SYSTEM

KEY

① , ② , ③ , ④ NEEDLE VALVES
⑤ , ⑥ , ⑦ , ⑧ STOP VALVES
⑨ , ⑩ , ⑪ , ⑫
⑬ ROTAMETER 0-100 l/min
⑭ ROTAMETER 0-200 l/min
⑮ ROTAMETER 0-25 l/min
⑯ ROTAMETER 0-75 l/min
⑰ ROTAMETER 0-10 l/min
⑱ ROTAMETER 0-4 l/min
⑲ ROTAMETER 0-2 l/min
⑳ ROTAMETER 0-2 l/min
㉑ GAS METER 50 l/min max
㉒ GAS METER 20 l/min max
㉓ GAS METER 20 l/min max
㉔ GAS METER 5 l/min max
㉕ MIXING VESSEL
㉖ U-TUBE MANOMETER PRESSURE INDICATOR
㉗ FLAME TRAP
㉘ HEAVY DUTY STOP VALVE
㉙ SAMPLING BOTTLE

FIG. 4   THE MICROWAVE CIRCUIT

(a) REFLECTED MICROWAVE SIGNAL

(b)

FIG. 5 SCHEMATIC DIAGRAM OF MICROWAVE SIGNAL FROM A BLAST
WAVE INITIATING A DETONATION
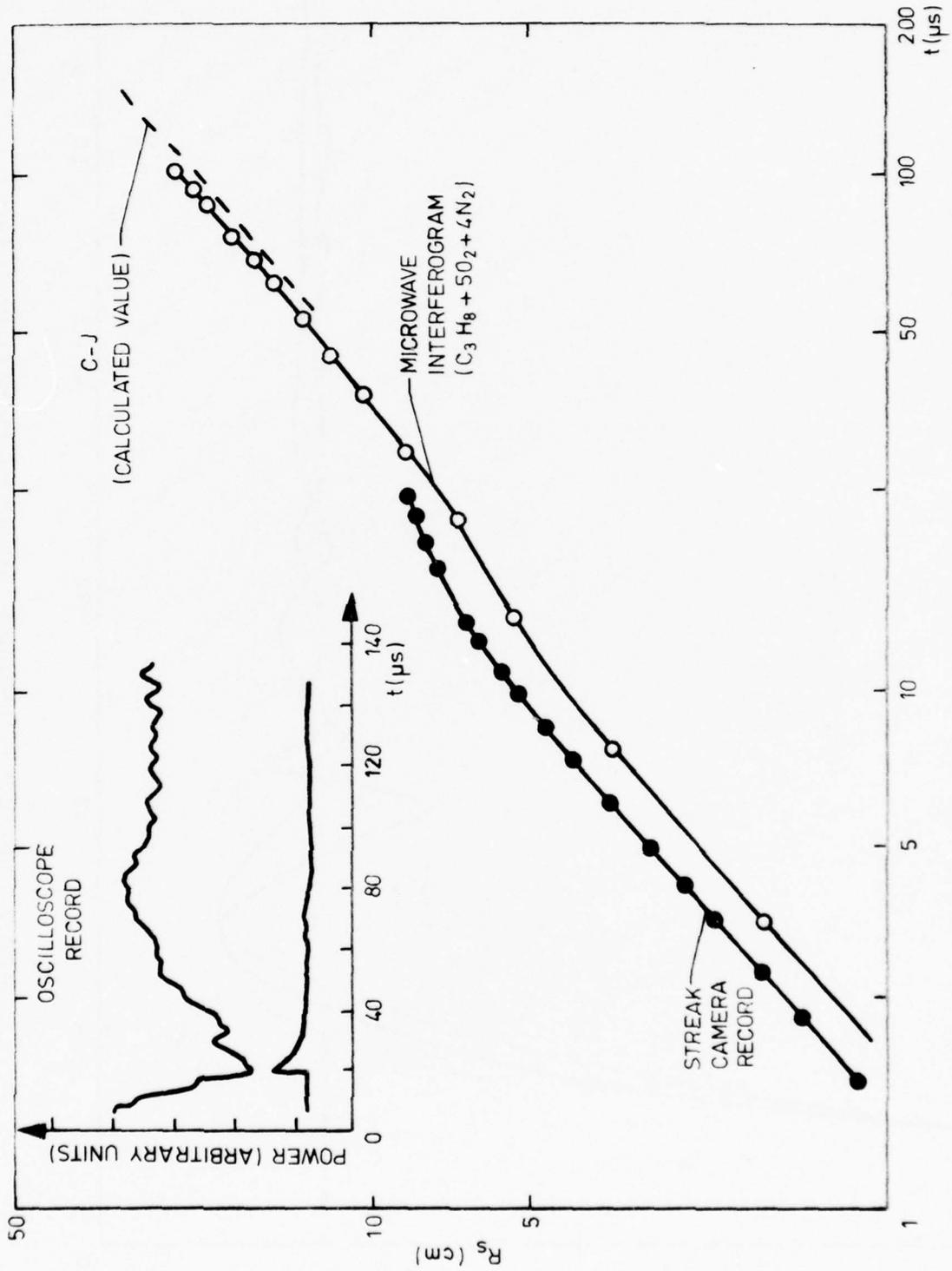
FIG. 6 MICROWAVE AND EVENT PROBE SIGNALS FROM 2·5g
INITIATION SOURCE IN $C_3H_8 + 5O_2 + 4N_2$

$C_3H_8 + 5O_2 + ZN_2$
$p_o = 0.1$ MPa

$Z = 6.12$
$Z = 6.00$
$Z = 6.90$

C-J
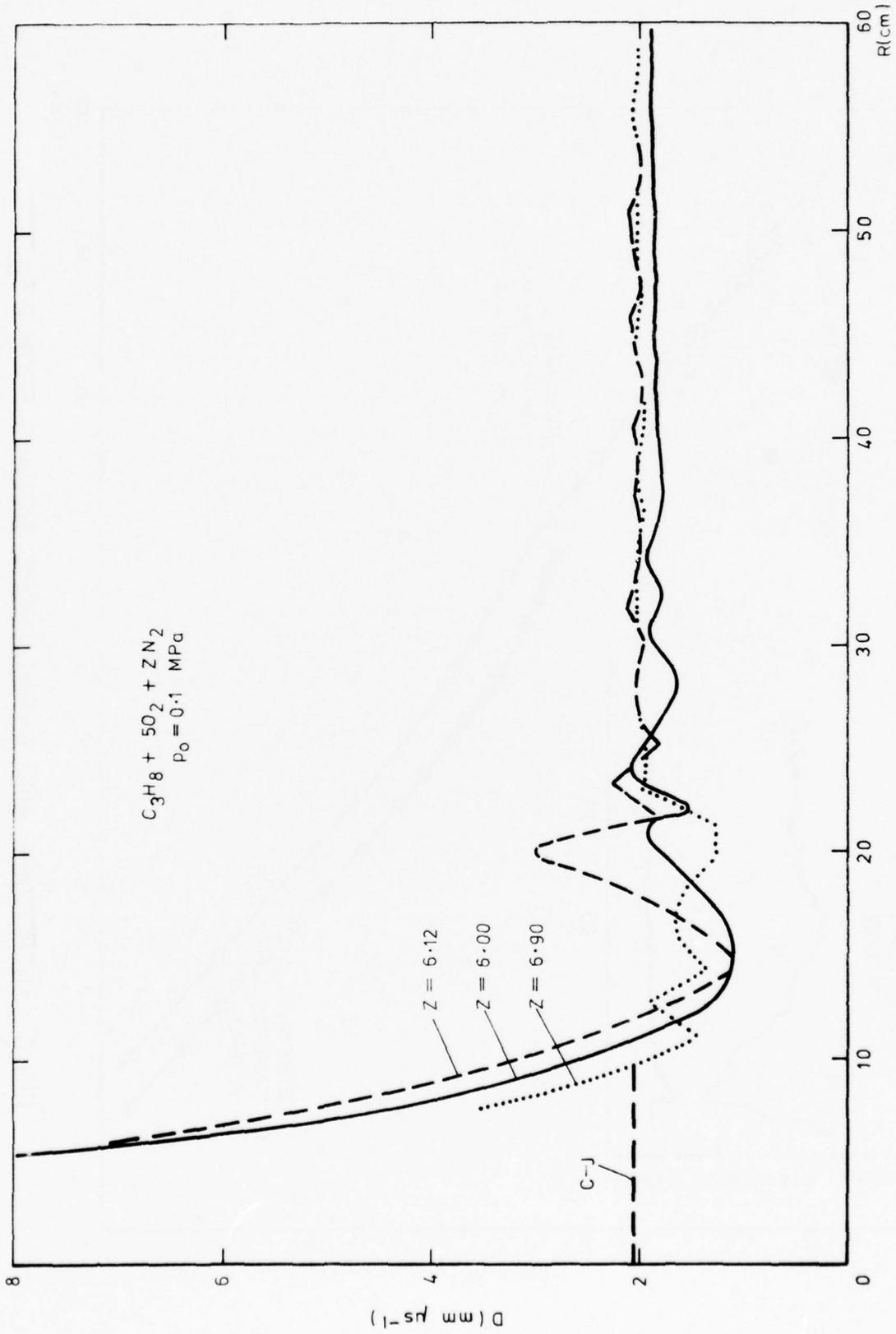
FIG. 7   VELOCITY-DISTANCE PROFILES IN MIXTURES OF
$C_3H_8 + 5O_2 + ZN_2$
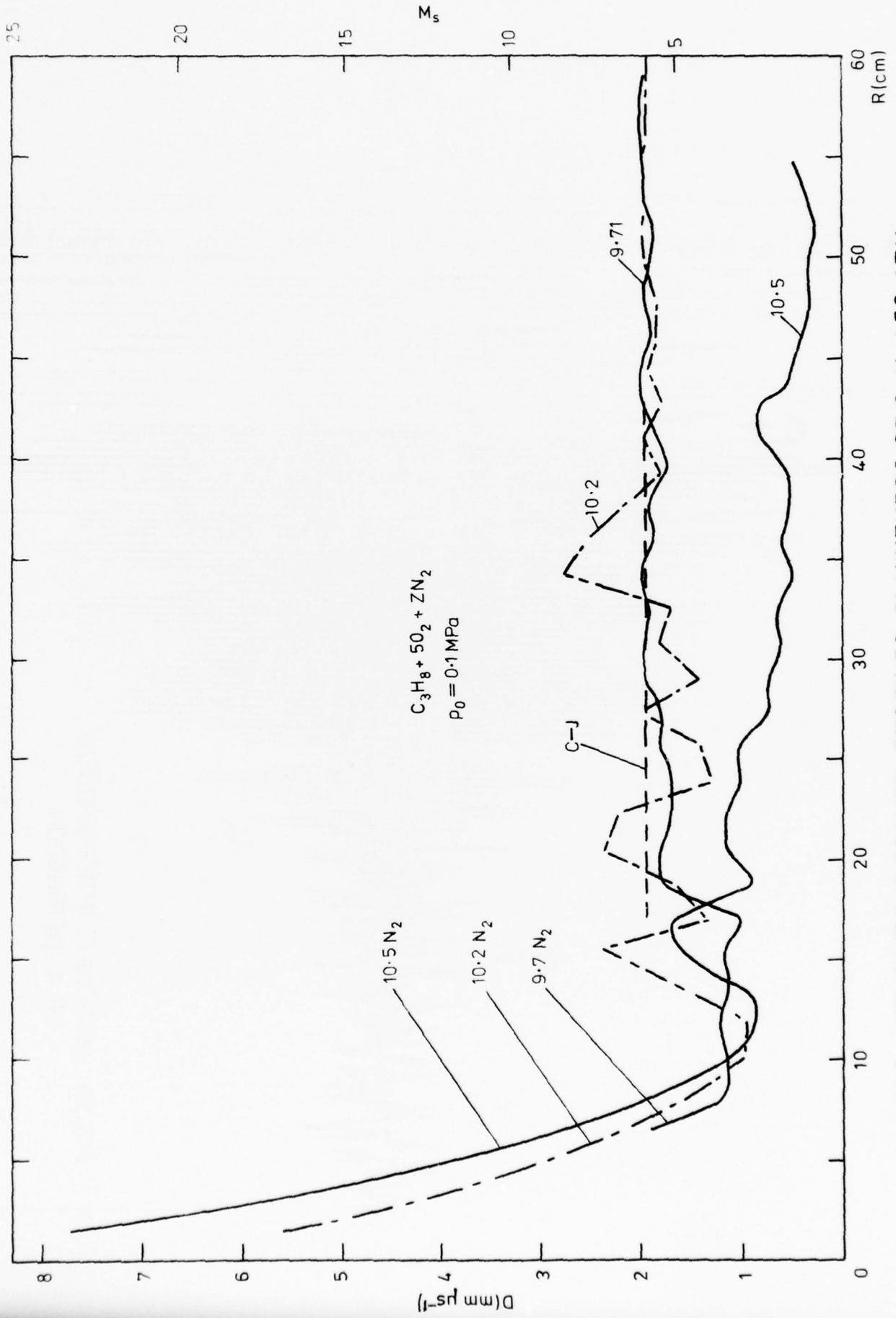
FIG 8 VELOCITY-DISTANCE PROFILES IN MIXTURES OF $C_3H_8 + 5O_2 + ZN_2$
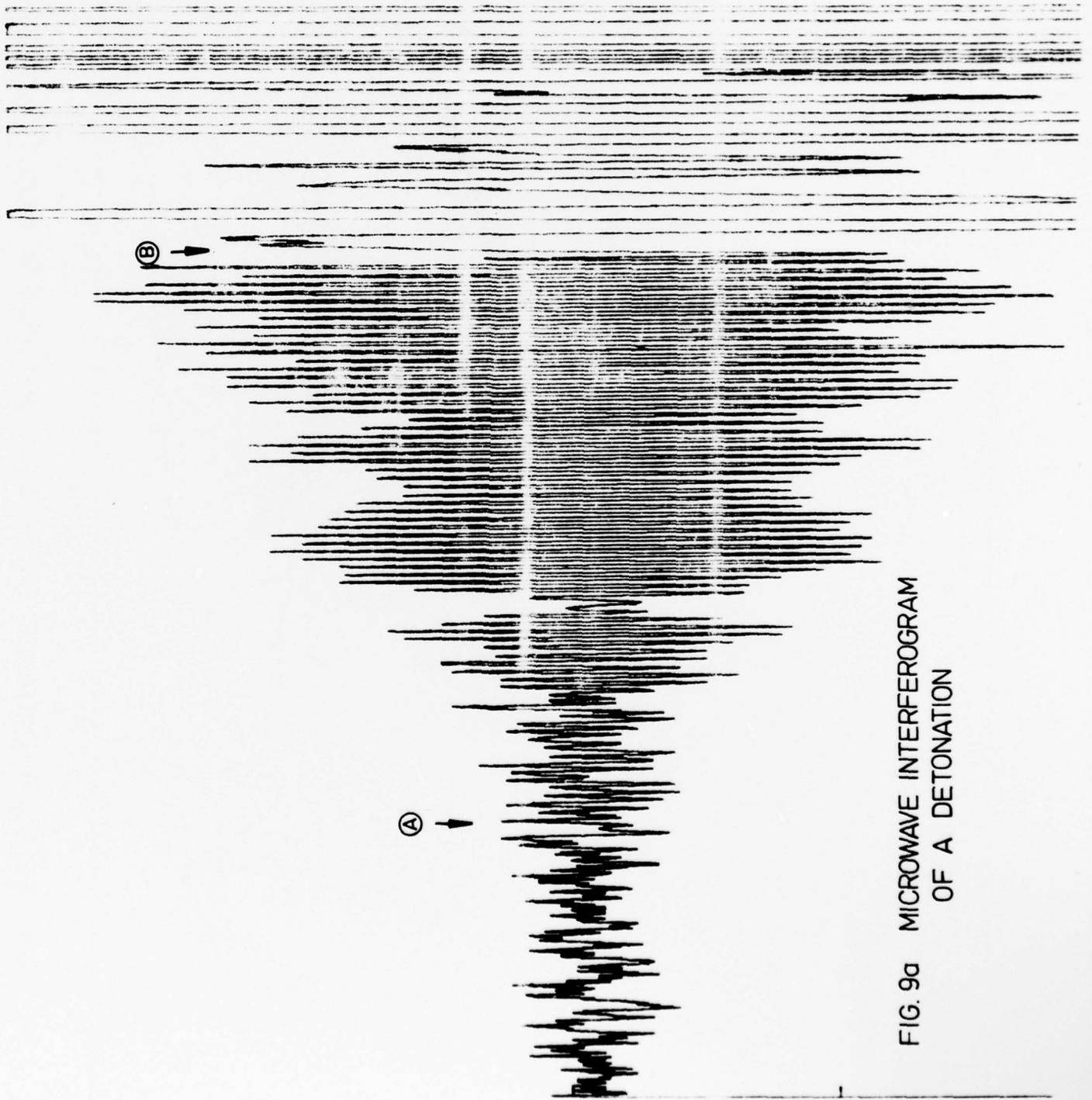
FIG. 9a MICROWAVE INTERFEROGRAM
OF A DETONATION
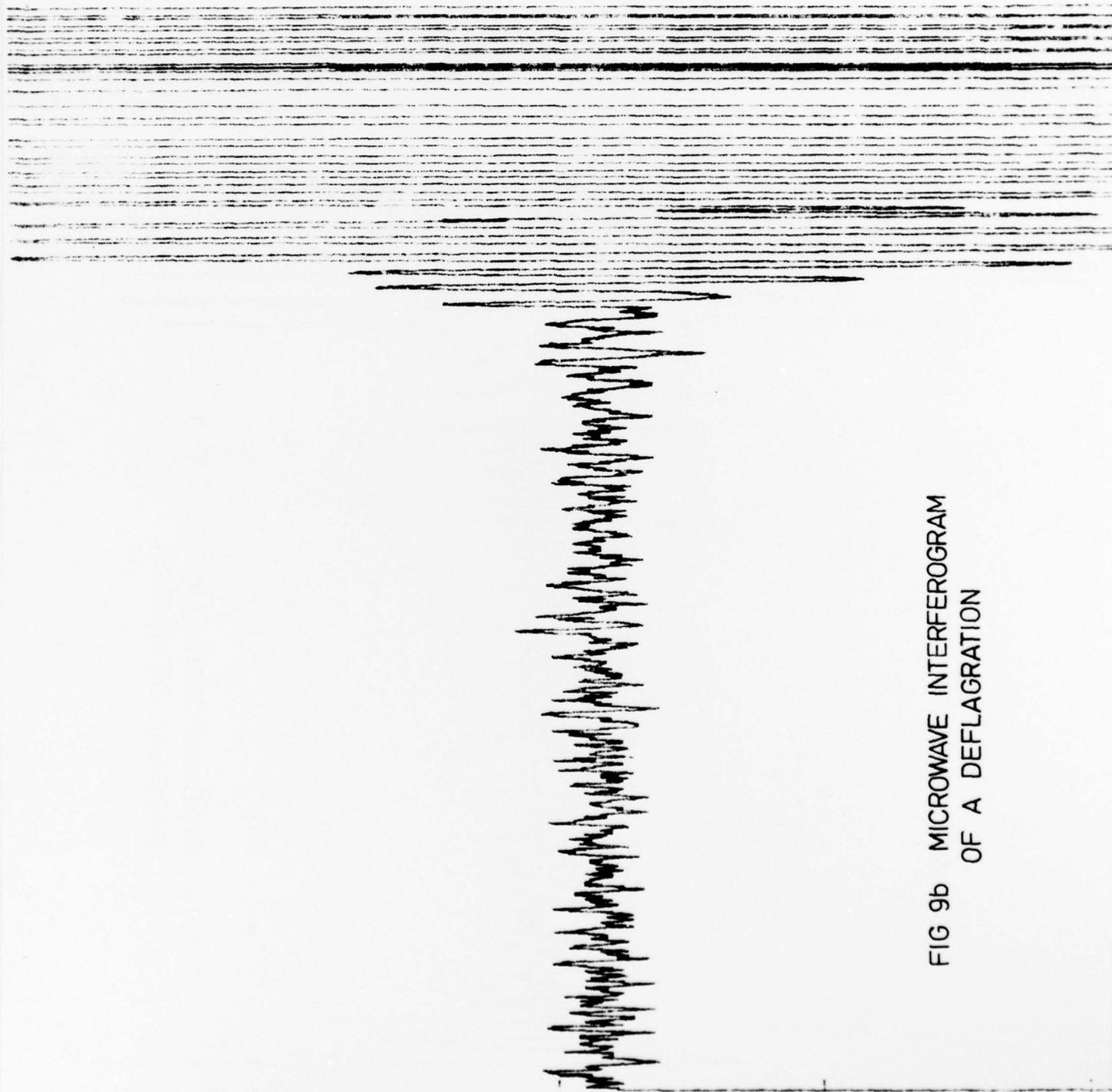
FIG 9b MICROWAVE INTERFEROGRAM
OF A DEFLAGRATION
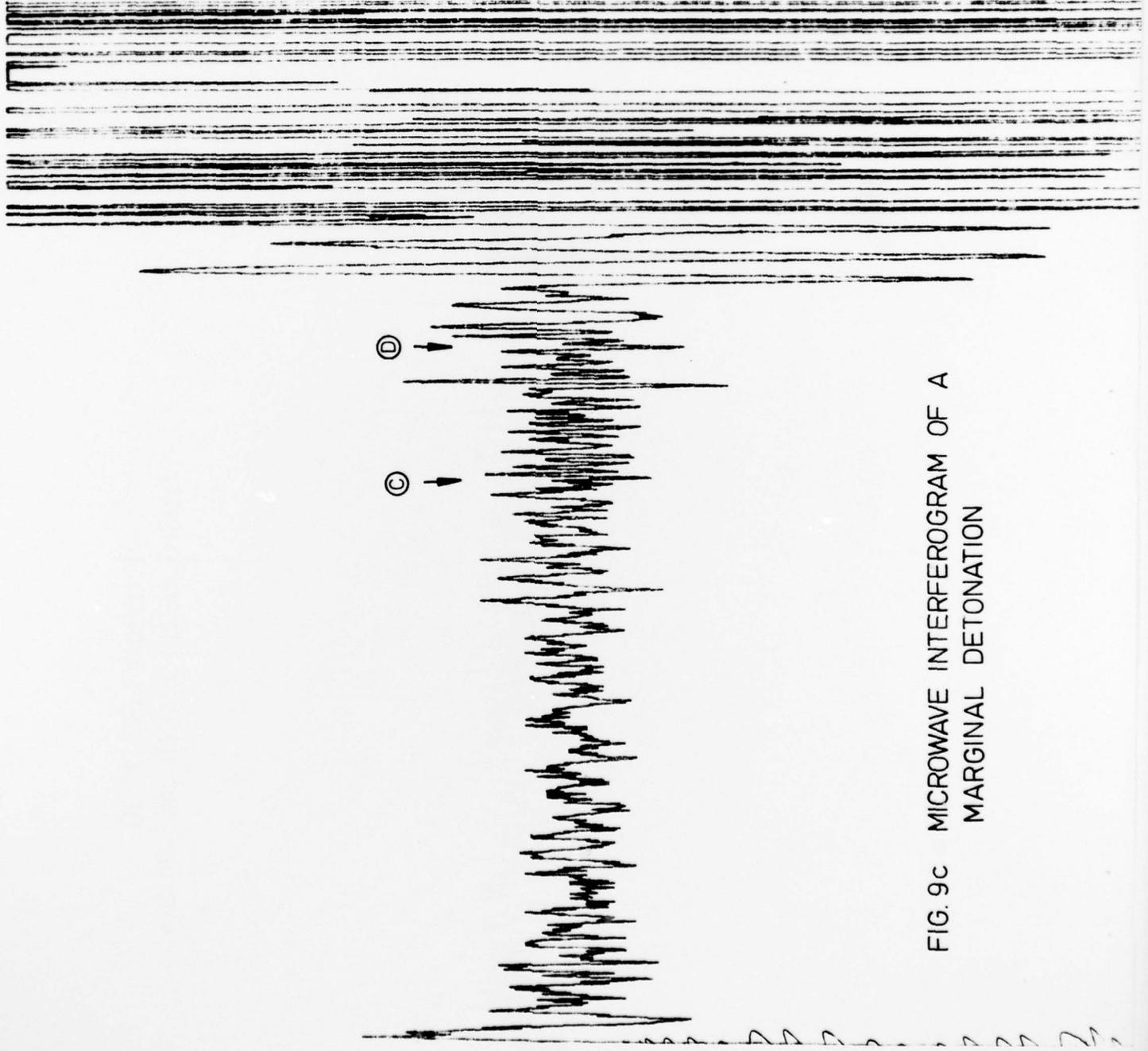
FIG. 9c MICROWAVE INTERFEROGRAM OF A
MARGINAL DETONATION

O DETONATION ESTABLISHED

X DETONATION FAILED

+ PRESSURE RECORDS INDICATED DETONATION,
   BUT MICROWAVE RECORDS DID NOT
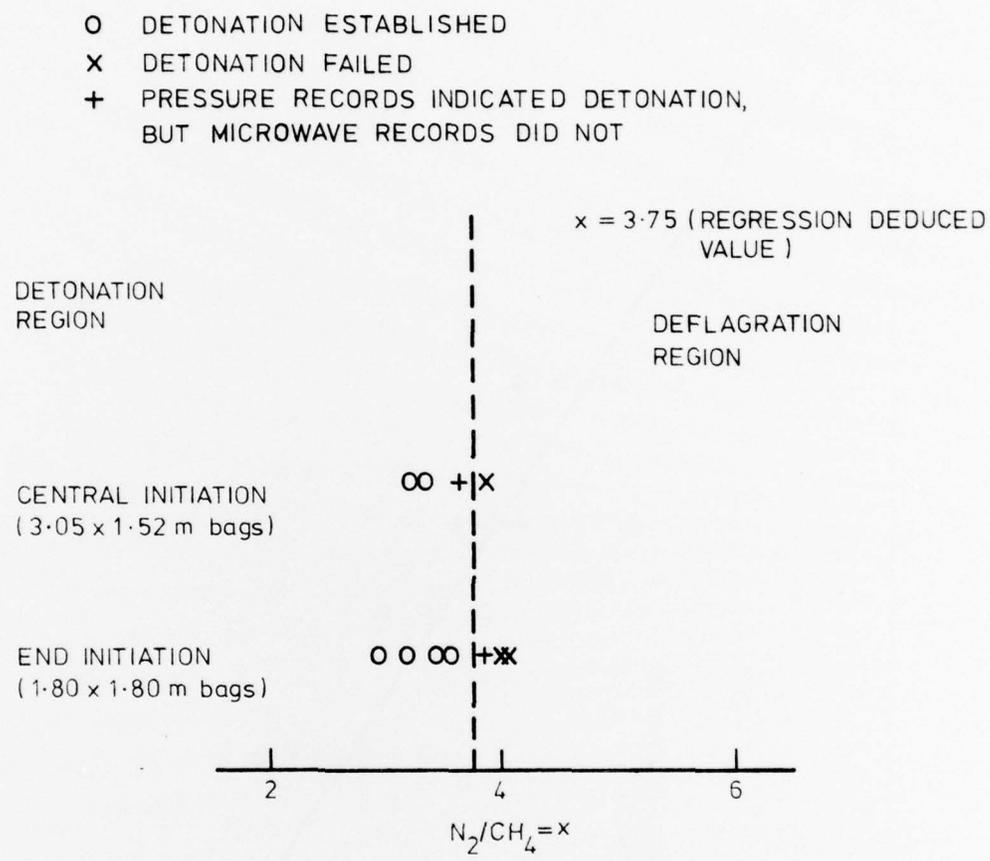
FIG. 10 CENTRAL AND END INITIATION OF GASEOUS
DETONATIONS IN POLYTHENE BALLOONS
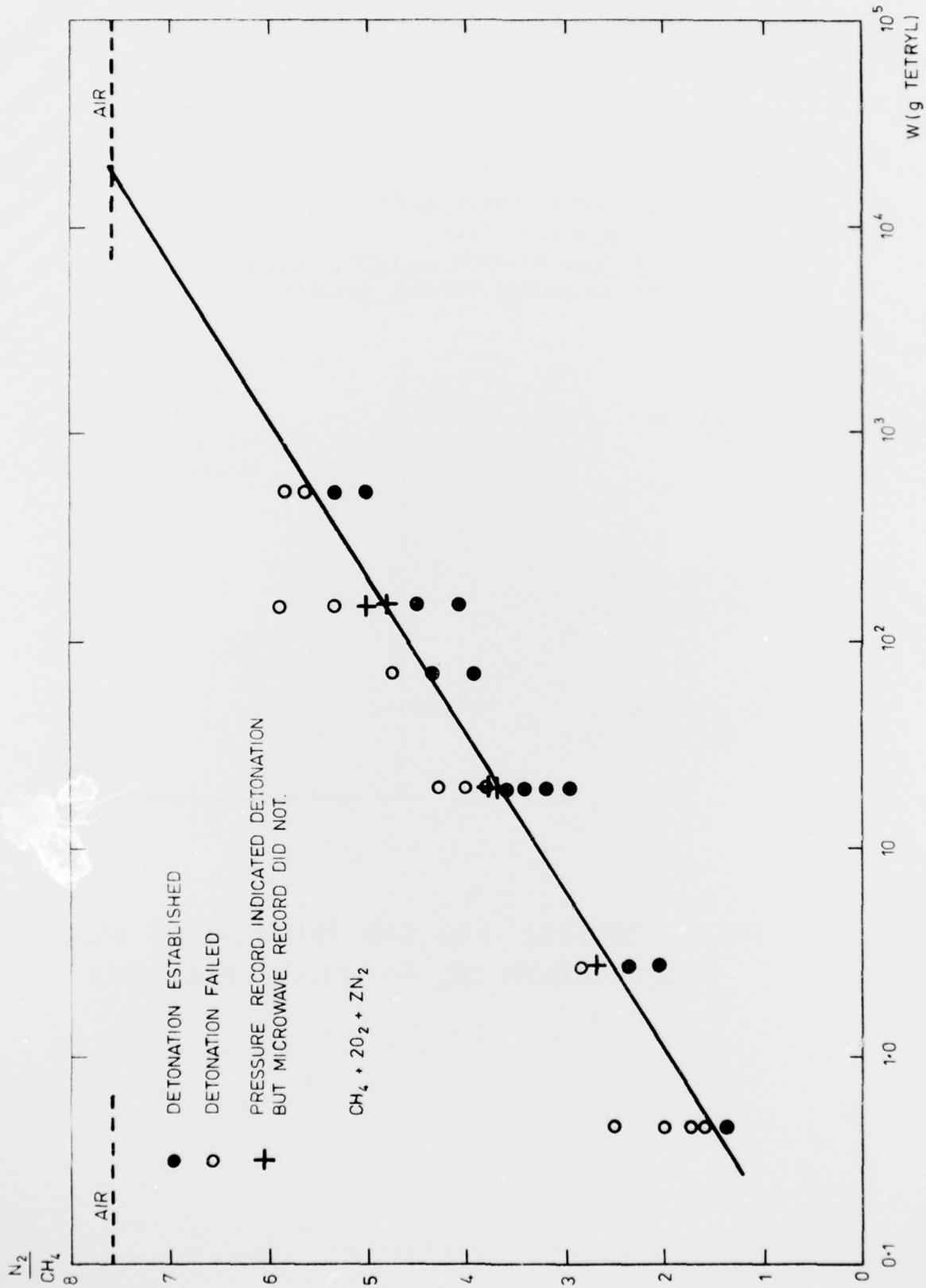
FIG. 11 DETONABILITY LIMIT IN $CH_4/O_2/N_2$ MIXTURES
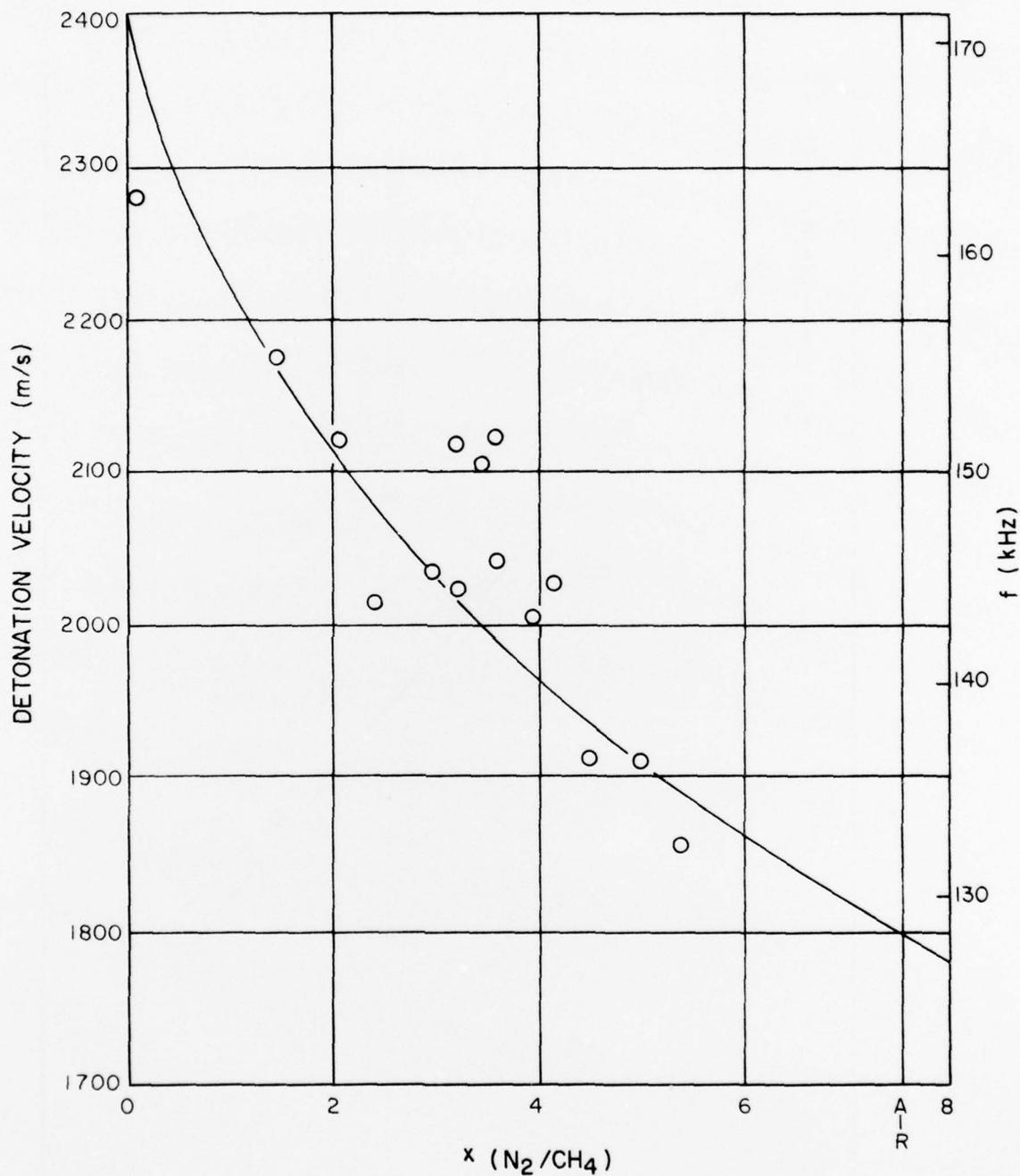
FIG. 12   DETONATION VELOCITIES IN CH_4/D_2/N_2 MIXTURES
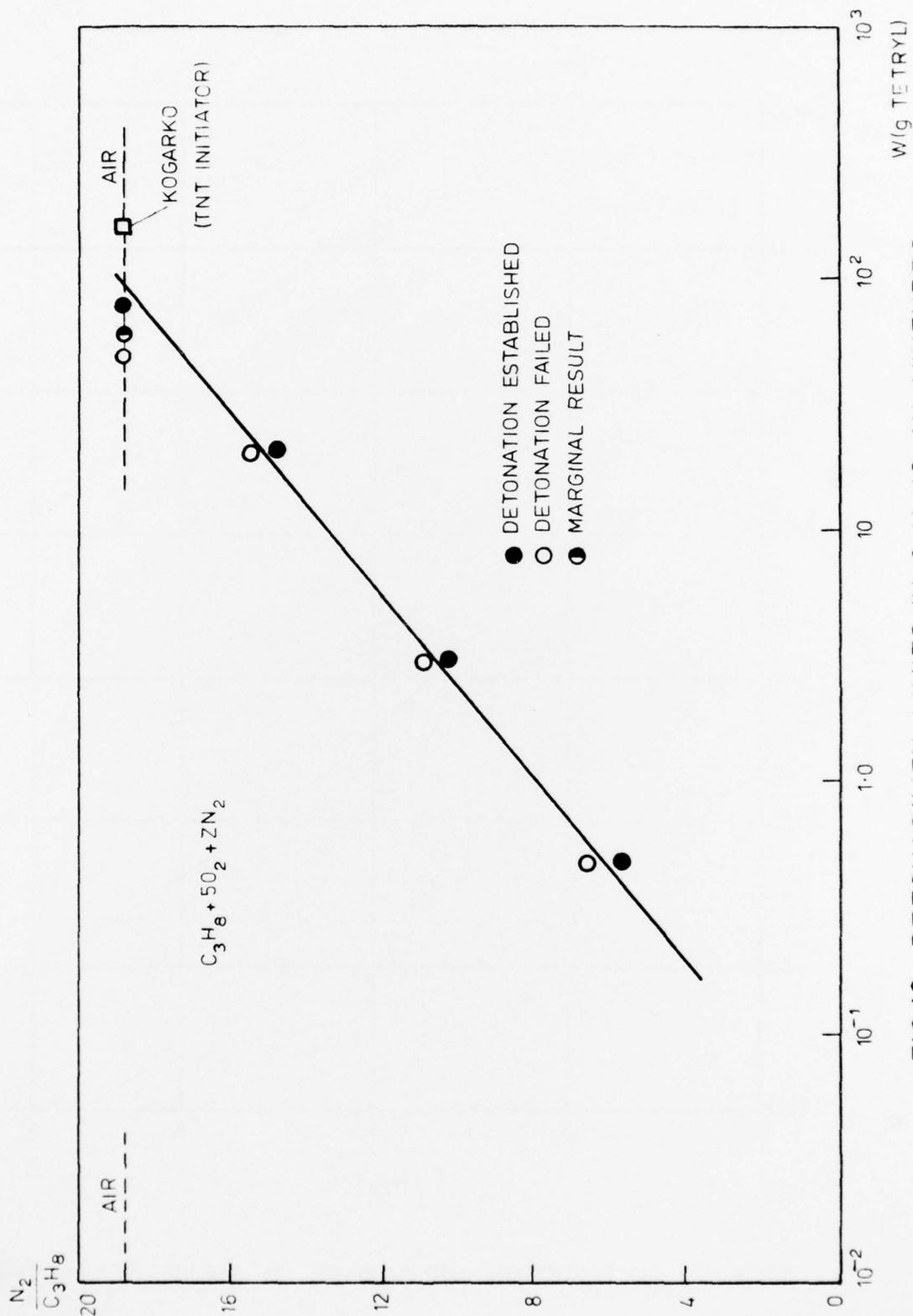
FIG.13 DETONABILITY LIMITS IN $C_3H_8/O_2/N_2$ MIXTURES
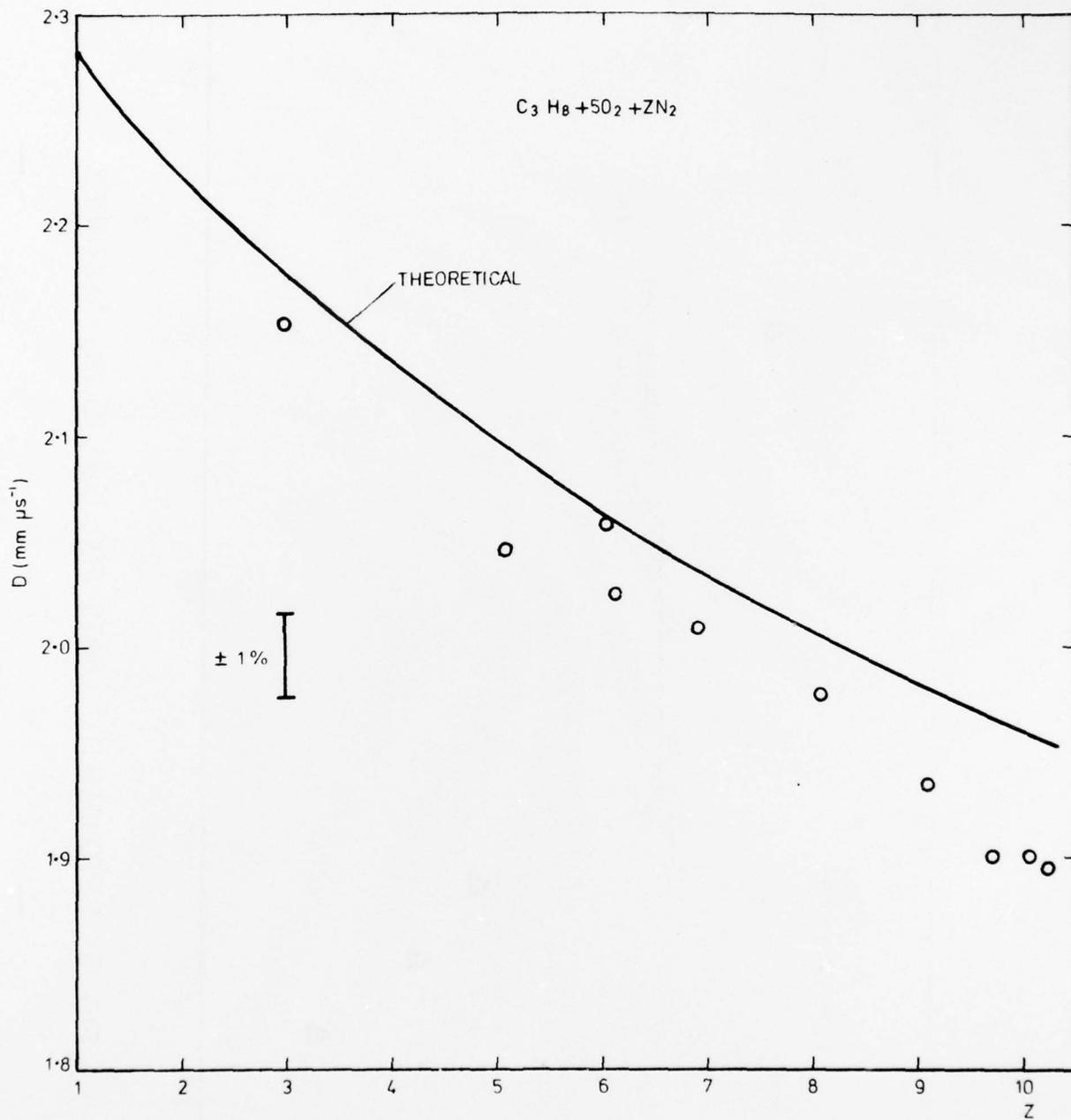
FIG. 14 DETONATION VELOCITIES IN $C_3H_8/O_2/N_2$ MIXTURES
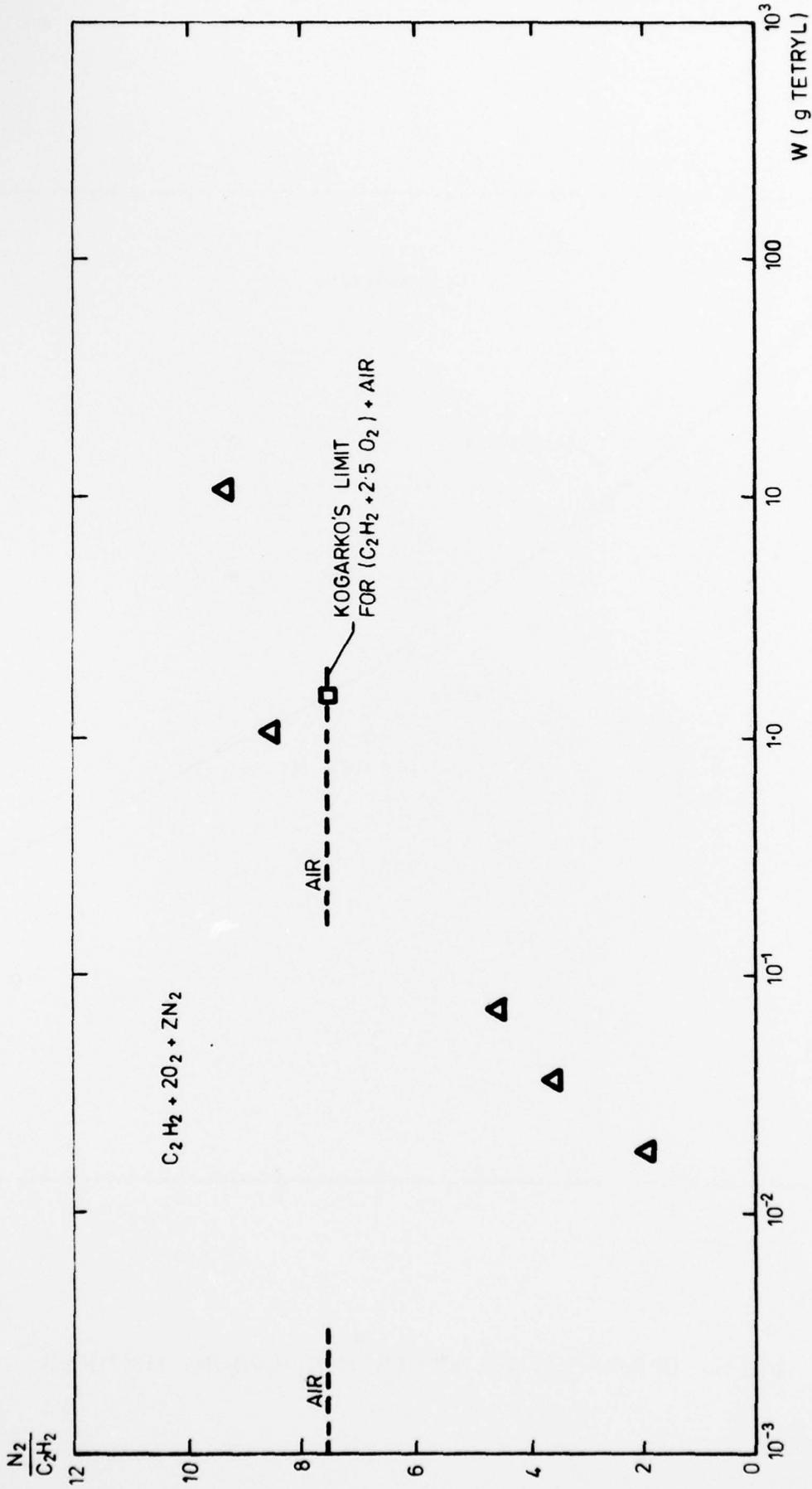
FIG. 15 DETONABILITY LIMITS FOR $C_2H_2/O_2/N_2$ MIXTURES
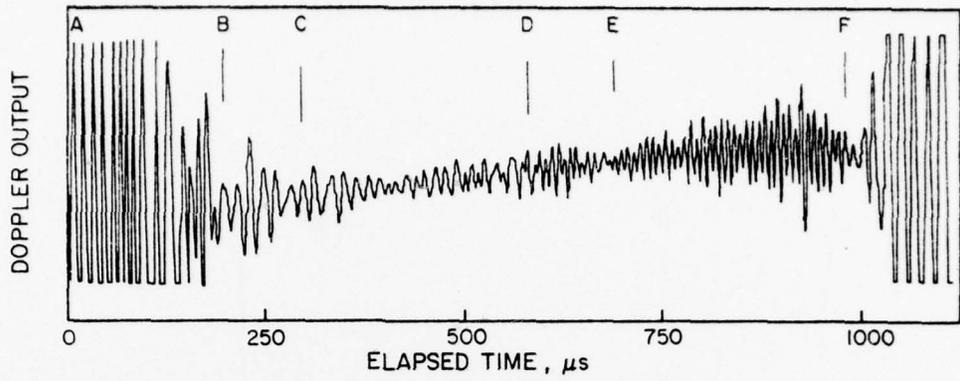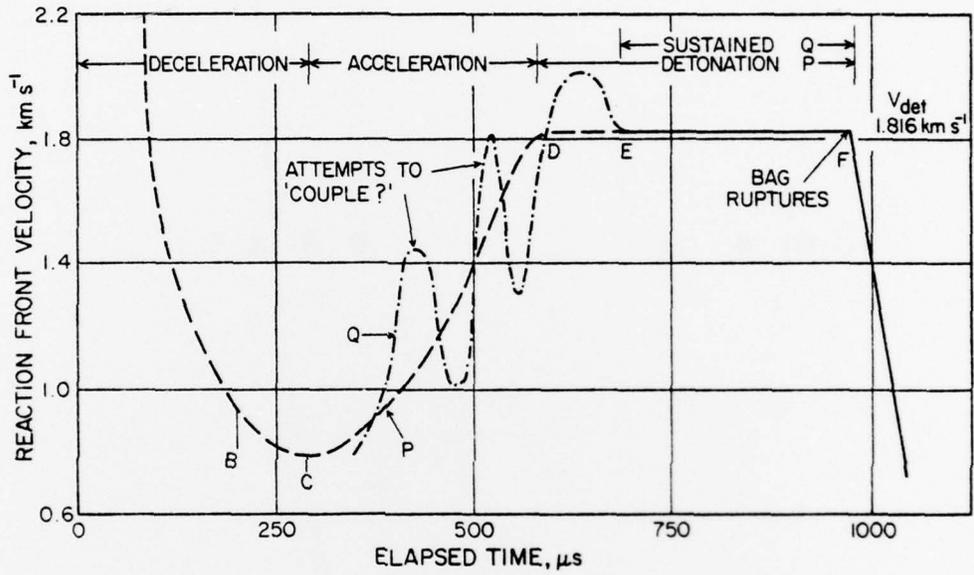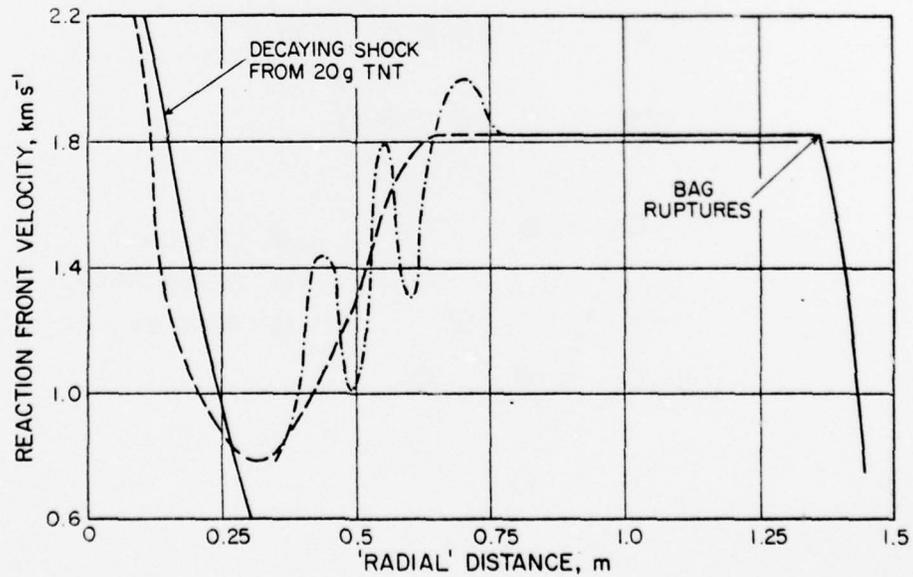
FIG. 16 (a) Microwave interferogram from an ethylene / air detonation close to
the limit of air detonability
(b) Interpretation of (a) as velocity, time history of reaction front
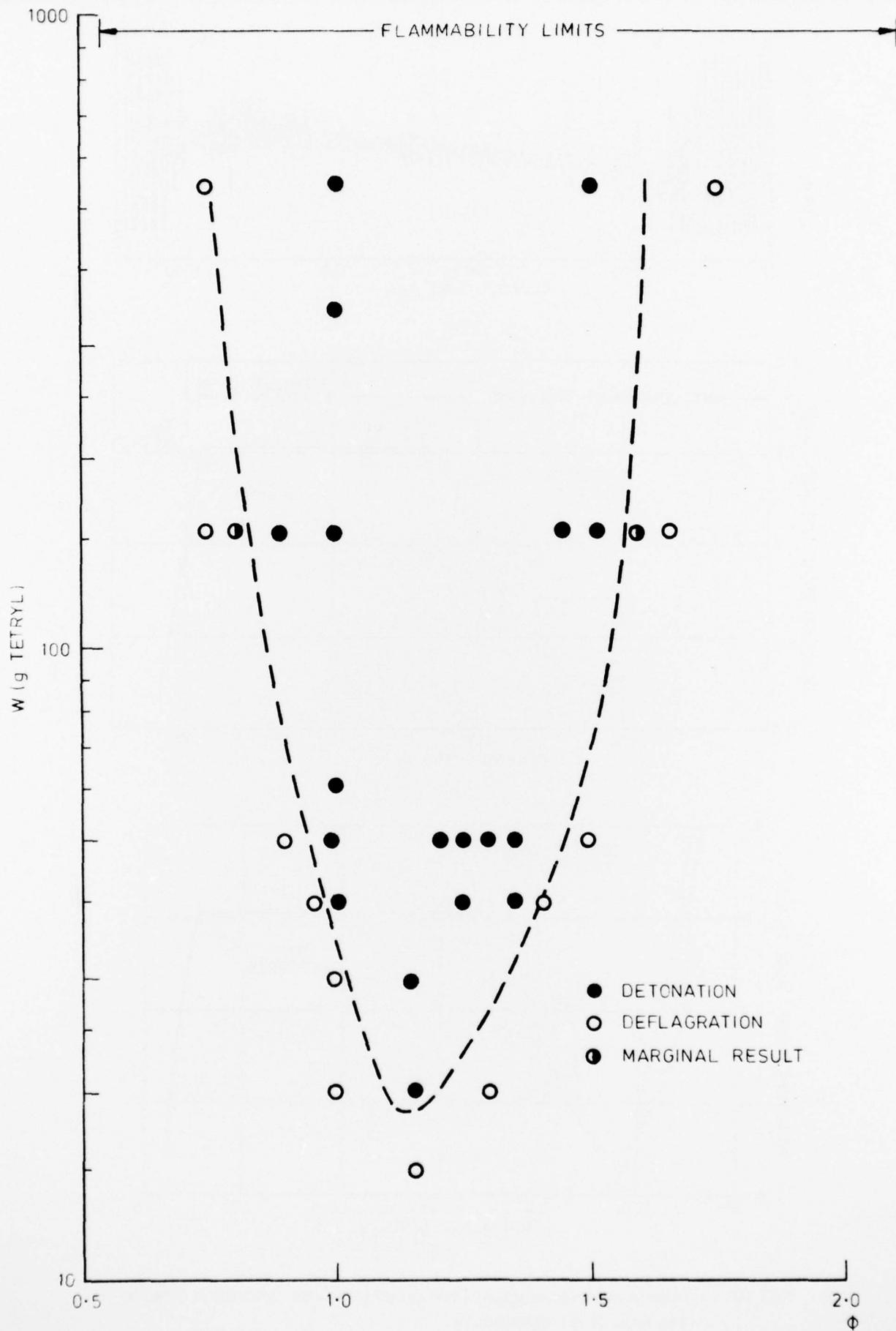(c) Interpretation of (b) as velocity, radial distance plot of reaction front
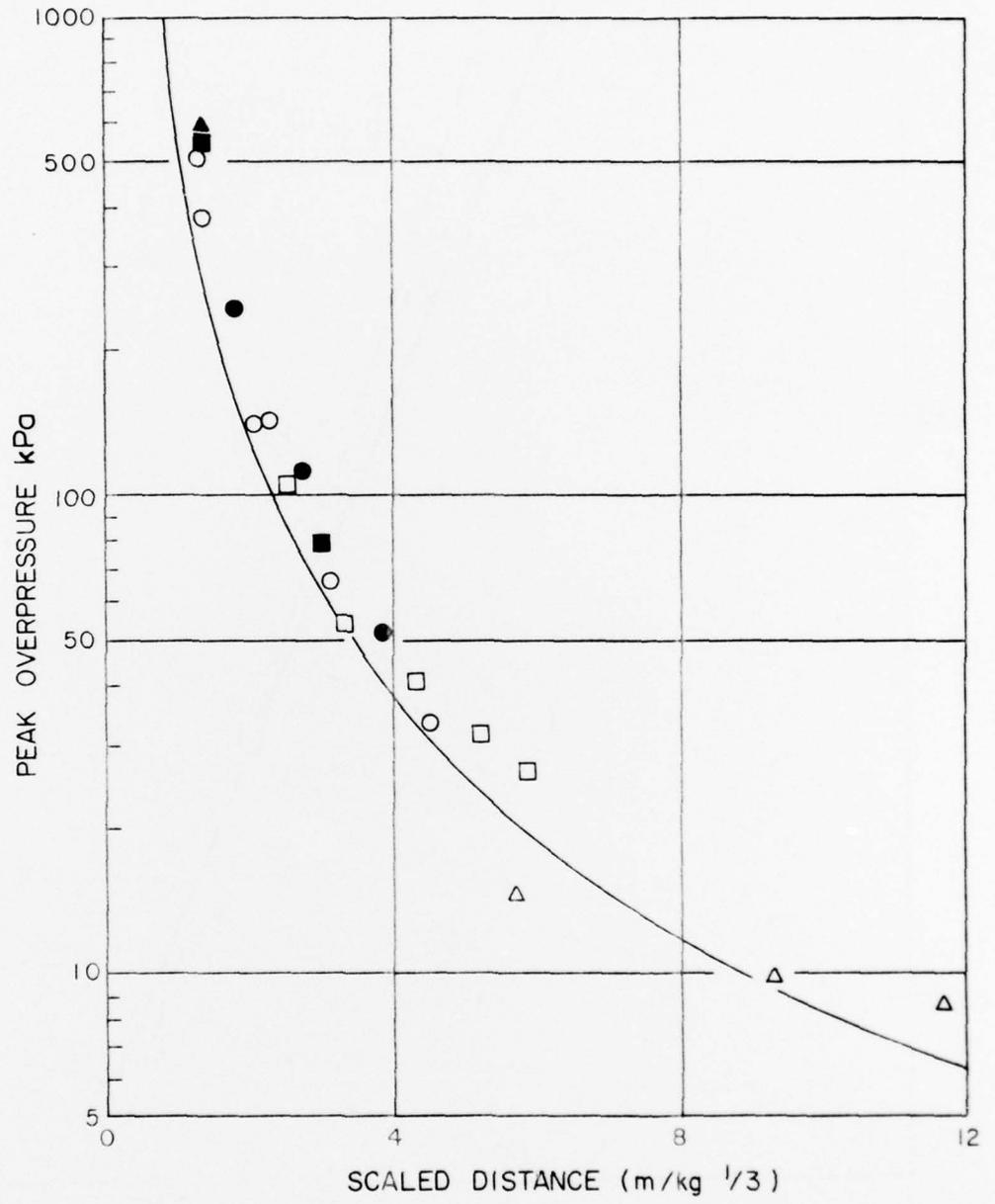
FIG.17   ETHANE–STOICHIOMETRIC FRACTION (Φ) IN AIR

FIG. 18 BLAST OF TETRYL PELLETS ALONE IN AIR
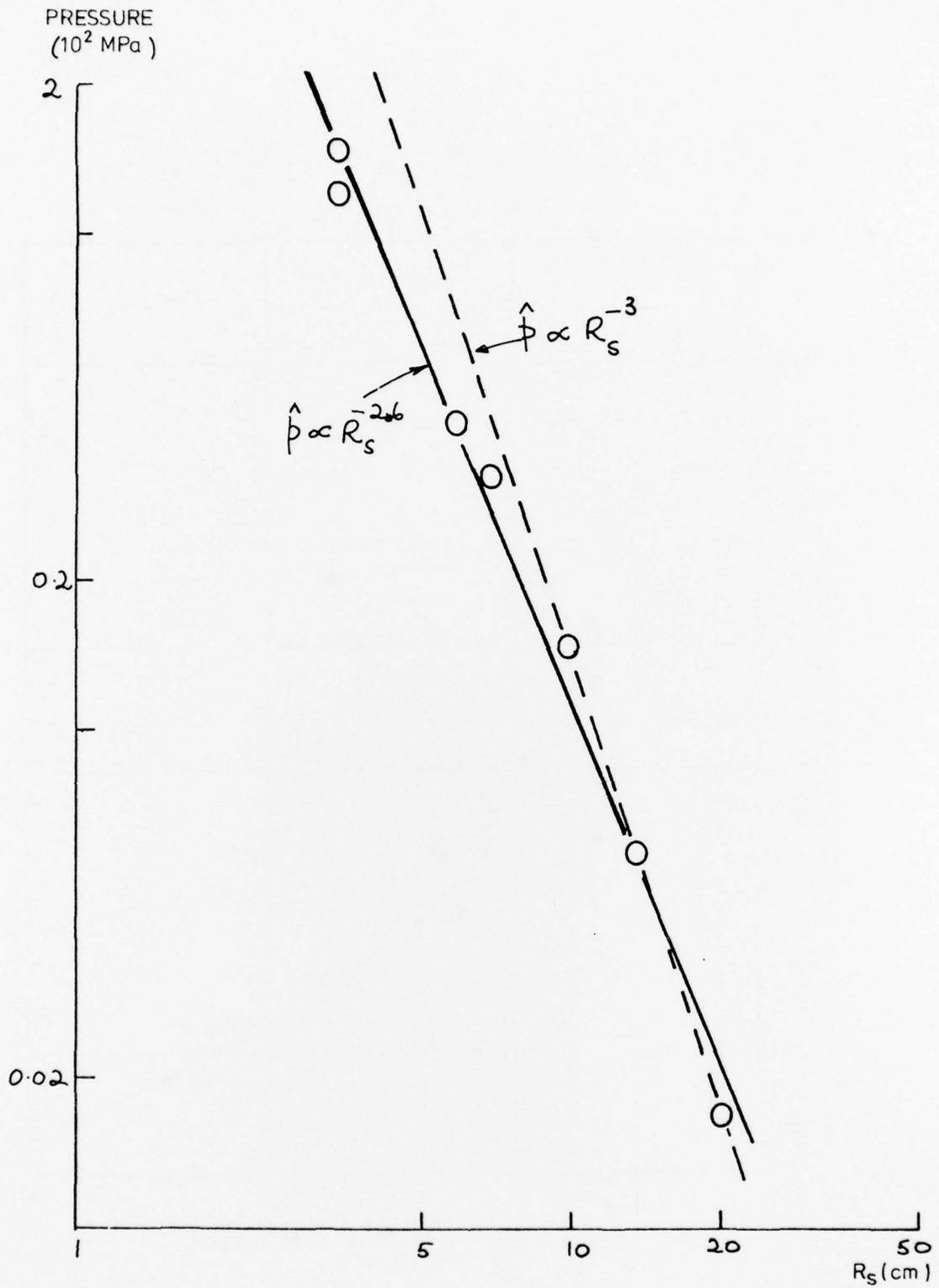TYPICAL RESULTS FOR MID AND FAR FIELD

FIG. 19   BLAST OF 2·5g TETRYL CHARGE ALONE IN AIR
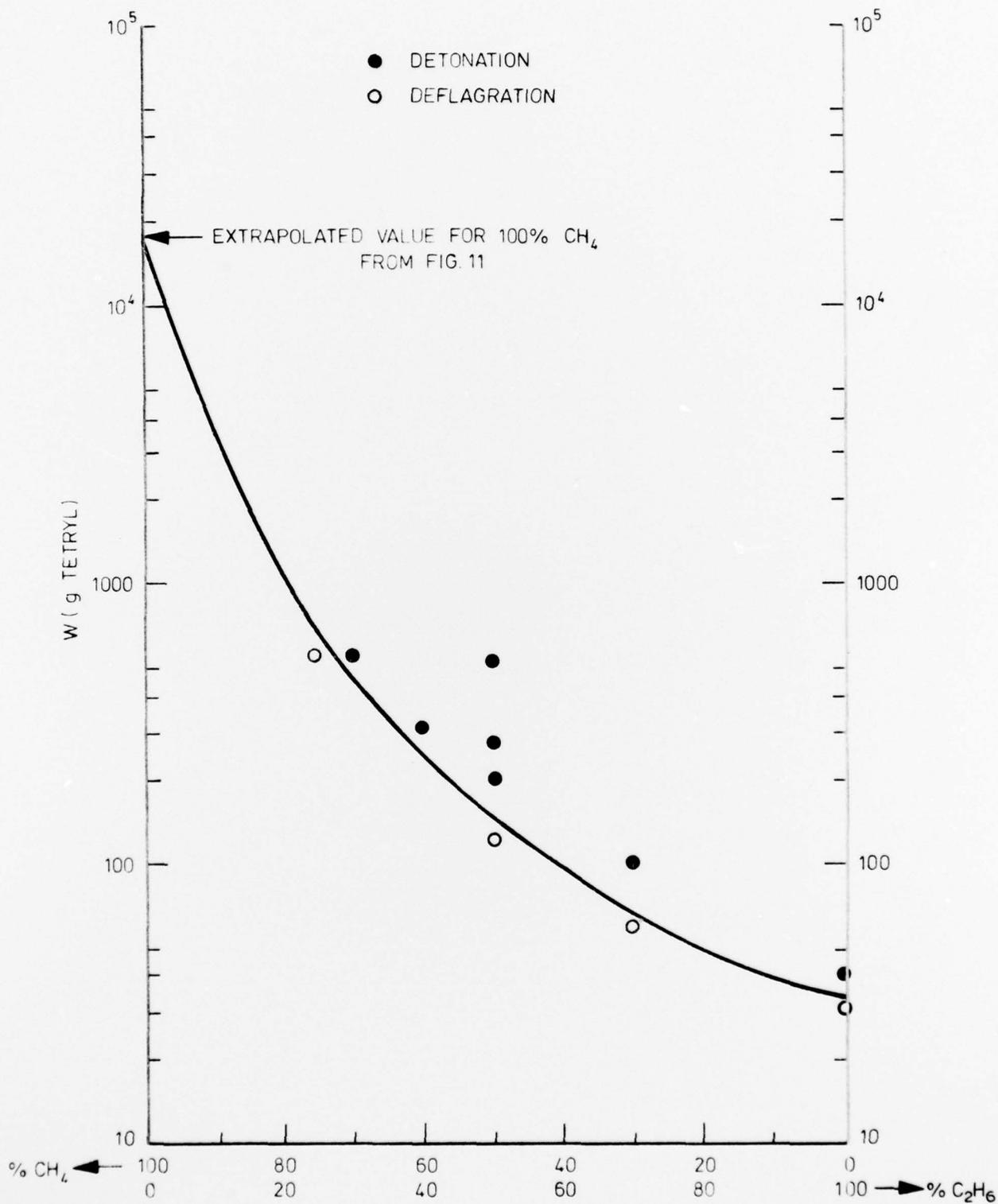TYPICAL RESULTS FOR NEAR FIELD

FIG. 20   CH₄/C₂H₆/AIR DETONABILITY

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1. DRIC Reference (if known)	2. Originator's Reference PERME TR 44	3. Agency Reference	4. Report Security Classification UNLIMITED
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5a. Sponsoring Agency's Code (if known)	6a. Sponsoring Agency (Contract Authority) Name and Location		

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7a. Title in Foreign Language (in the case of translations)

7b. Presented at (for conference papers). Title, place and date of conference

8. Author 1. Surname, initials Hooper G	9a Author 2	9b Authors 3, 4...	10. Date 9/78	pp 56	ref 31
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15. Distribution statement

Descriptors (or keywords)

Explosions, Aliphatic acyclic hydrocarbons, Air, Detonation, Sensitivity, Initiation

(TEST)

Abstract An experimental technique is described whereby the sensitiveness of a number of hydrocarbon/air mixtures is assessed in terms of direct detonative initiation from solid explosive charges. A microwave interferometer is used to monitor continuously the propagation of the reaction zone in the gaseous system over a path length of several metres, and to give a reliable distinction between detonation and deflagration. The hydrocarbons acetylene, ethylene, ethane, propane, butane, isobutane, and methane are ranked in order of the sensitiveness of the stoichiometric fuel/air mixtures. The critical initiation energy of ethane is measured as a function of fuel/air stoichiometry. The minimum initiation energy for various stoichiometric methane/ethane/air is assessed. A brief literature survey is included.