THE EXPLOSIBILITY OF SOME UNSATURATED C_4 HYDROCARBON FRACTIONS.

F.W.S. Carver*, D.J. Hards* and K. Hunt*

The decomposition characteristics of some unsaturated C_4 hydrocarbon fractions containing vinylacetylene have been examined in both the gas and liquid phases using shock wave and exploding wire initiation. The mechanism of decomposition was found to depend on the energy of initiation and its time of application. Decomposition arising from shock wave initiation occurred only when the mixture was sufficiently energetic to support a detonation wave. With exploding wire initiation, decomposition in the form of a deflagration reaction occurred in less energetic systems. In most cases this led to an explosion which was possibly detonative in character.

INTRODUCTION

On October 23rd 1969, there was an explosion in the butadiene refining unit at Union Carbide's Texas City olefins complex. Much of the butadiene unit was destroyed and the adjacent large ethylene plant was severely damaged. The explosion occurred in a refining column that was used to remove butadiene from other C_4 components, (eg. vinylacetylene, ethylacetylene) and C_5 components.

Reports of the investigation into the cause of the accident were published in 1970 and 1971 (1,2,3).

The main conclusion reached was that a leaking valve assembly at the top of the refining column, while the column was under total reflux, caused the liquid level in the base of the column to fall and the overall concentration of vinylacetylene in the column to rise. A deflagration started in the base of the column and spread upwards. When the high pressure/high temperature front encountered a sufficiently high concentration of vinylacetylene, the liquid vinylacetylene detonated.

Although much work has been published on the explosion limits of vinylacetylene when in admixture with air or oxygen (4,5,6,7,8,9) and some on the effects of the level of initiation energy on the propagating self-decomposition of vinylacetylene as a function of pressure and the tube diameter (10), little has been reported on the effects of other unsaturated C_4 hydrocarbons on the self-decomposition limits. Some vapour phase decomposition work was done in support of the accident investigation at Texas City (1) but this was not

* Ministry of Defence (PE), EM2 (Home Office) Branch, RARDE, Royal Arsenal East, LONDON, SE18 6TE.

sufficiently comprehensive to answer all the questions being asked in Europe about the safety of the system.

It was because of this situation that the B.P. Chemical International Ltd approached the EM2, RARDE laboratory with a view to sponsoring work not only on behalf of themselves, but also on behalf of Shell Internationale Chemie Maatschappij NV (BICM), Badische Anilin-Soda-Fabrik A.G (BASF), and Imperial Chemical Industries Ltd (ICI). The aim was to obtain more experimental information about the explosion limits of vinylacetylene in both the gaseous and liquid phases under conditions representative of those used in their refining complexes.

The experimental programme that ensued was drawn up and regularly monitored at joint meetings held with representatives of the four industrial firms. At the same time as this work was proceeding, a great deal of complementary vapour phase work was being carried out in the BASF laboratories (11). These results were made freely available and will be discussed.

EXPERIMENTAL

General

The most urgent aspect of this investigation was to establish the absolute limits for self-decomposition of vinylacetylene/1,3-butadiene mixture in both the vapour and liquid phases at 52°C and ambient temperature respectively. Previous work in this laboratory in which the propagating self-decomposition of acetylene had been studied suggested that this could best be done by using a detonative ignition (12). It was decided that a No.8 detonator would provide a suitable ignition system for this part of the investigation. Subsequently the effects of reducing the level of initiation energy, increasing the initial temperature and the addition of other unsaturated C_4 hydrocarbons on these explosion limits were determined. The final part of this work was an examination of the effect of replacing 1,3-butadiene with acetonitrile in the liquid phase system.

In the vapour phase studies, the weight of the mixture used was calculated to be approximately twice that which would give the saturated vapour pressure in the explosion vessel.

Materials

Vinyl Acetylene. Vinylacetylene was supplied by the Dupont Company, Northern Ireland, as a 50% (W/W) solution in xylene. On average, the regenerated vinylacetylene was found to be 98-99% pure.

1,3-Butadiene. Commercial 1,3-butadiene was supplied by B.P. Chemicals (UK). Analyses done in the B.P. laboratories gave the 1,3-butadiene content as 99.4% (V/V).

Industrial Gas Mixtures. Two samples of a mixture of vinylacetylene/1,3-butadiene/1,2-butadiene/ethylacetylene dissolved in xylene were supplied by ICI. The compositions were found to be

	Mole %	
	Sample I	Sample II
Vinylacetylene	41.7	72.3
1,3-butadiene	32.9	14.3
1,2-butadiene	14.2	6.7
Ethylacetylene	11.2	6.7

Acetonitrile. A sample of acetonitrile, ex Fluka A.G. was supplied by B.P. Chemicals (UK) together with the following analysis

| Acetonitrile | 99.83% |
| Water | 0.16% |

Explosion Vessels. (Figs 1 and 2)

Gas Phase Studies. The vessel was essentially a length of steel tubing, 159 mm OD, 102 mm ID closed off at either end by 51 mm thick steel plugs. These plugs were screwed and then welded in place. The overall length of the vessel was 350 mm and its capacity was 2.6 l. One of the end plugs was drilled and tapped to accept the firing plug assembly and the other to accept a 38 mm diameter bursting disc holder. Small holes were drilled and tapped into the walls of the vessel for the inlet and outlet pipes and the pressure gauge. Halfway through the experimental programme, two more entries were made for a thermocouple and a strain gauge. These were positioned as close to the bursting disc assembly as was practical.

Liquid Phase Studies. This type of vessel was designed to be disposable and was made from cold drawn steel tubing, 330 mm long, 39 mm OD and 25 mm ID. The lower end was closed by brazing in a detonator holder, and the upper end was fitted with a heavy duty screw-on cap. Just below the end cap, the vessel was tapped and a small side arm of 6 mm OD steel capillary was welded in position. This provided the entry for filling the vessel. Preliminary experiments with this type of vessel filled with water to a depth of 75-100 mm above a No.8 detonator showed that the hydrostatic force produced by an exploding detonator was sufficient to split the vessel. Hence during normal firings, the vessels were supported in a heavy steel block to a height at least equivalent to the anticipated liquid level.

Ignition Systems.

Detonative Ignition. Commercial No.8 aluminium sheathed flat-based detonators were used. In the vapour phase experiments, these were found to cause no visible damage to the bursting disc, whereas concave based detonators produced a jetting effect and bursting disc damage by direct fragment impact.

Fusing Wire Ignition. A 13 mm length of 0.05 mm diameter 80/20 platinum/iridium wire was fused by either a 0.5J or 100J discharge from a capacitor bank.

Filling Procedures. (Figs 3 and 4)

Approximate quantities of the various materials were distilled under vacuum into weighed stainless steel reservoirs.

Vapour Phase Vessels. The charge reservoir was connected via a manifold to the reaction vessel which had been previously purged with oxygen free nitrogen and

evacuated. The reservoir was heated with an external steam coil and the reaction vessel was cooled in an ice/water bath and then the transfer mainly via the liquid phase was allowed to take place. After closing off the reaction vessel from the manifold, it was raised to the required firing temperature in a waterbath and allowed to equilibrate for 20 minutes. Immediately prior to firing, a sample of the vapour was taken for gas chromatographic analysis, and the pressure inside the vessel was measured.

Liquid Phase Vessels. A small sample of the liquid mixture was taken from the reservoir for analysis before it was connected via a manifold to an evacuated explosion vessel, cooled with a solid carbon dioxide/acetone mixture. The geometry of the system was arranged such that there was a direct liuqid transfer into the explosion vessel.

Analysis of Samples

The reactant samples were analysed by gas chromatography using a Pye 104 gas chromatograph. The conditions used were:-

Column	: 1.5 m glass column filled with 10% carbowax 400 on chromasorb
Column Temperature	: $25^{o}C$
Detector	: flame ionisation

Pressure Measurements

In the vapour phase experiments, the pre-firing pressure was measured with a Bourdon tube gauge connected to the vessel by a stop valve. To overcome the problem of vapour condensing in the gauge, it was pressurised with nitrogen before each experiment to a pressure slightly above that which was anticipated. Although this meant that nitrogen was released into the explosion vessel when the stop valve was opened, the quantity was considered sufficiently small (~2-3 ml at N.T.P.) to have little or no effect on the experiment.

Pressures in the vapour phase were measured during the decomposition by a diaphragm pressure strain gauge connected to a galvanometer recorder using ultra-violet light sensitive paper. The response time of this system was better than 10 milliseconds.

Temperature Measurements

A chromel/alumel thermocouple, projecting 20 mm into the gas space of the vapour explosion vessel was used. The output was fed to a second channel of the galvanometer recorder. The response time was difficult to assess, but from comparison of records, it appeared to be little different to the pressure response time. A typical pressure/temperature record is shown in figure 5.

<div align="center">RESULTS AND DISCUSSION</div>

Vinylacetylene/1,3-Butadiene Mixtures. (Tables 1 & 2)

Explosion limits found for this system may be summarised as follows:-

Phase	Initial Temperature $^{\circ}C$	Initial Pressure KN/m^2a	Initiation	Induction Period S	Limit mole % vinylacetylene
Gas	52	550	Detonator	0	62
Gas	52	570	0.5J	2.5	47
Gas	52	570	100J	2	41
Liquid	25	-	Detonator	0	40-42
Liquid	52	-	Detonator	0	40-42

The large difference between the explosion limits in the gas phase for detonative ignition and hot wire ignition, together with the existence of an induction period in the latter case suggest different mechanisms of decomposition. With shock initiation, it would seem that decomposition takes place only when the mixture is sufficiently energetic to support a detonation wave. On the other hand, with exploding wire initiation, the system has to be sufficiently energetic to support a slow reaction or deflagration initially. The effect of this slow reaction is to cause an increase in temperature and pressure of the mixture to a point where they can undergo very rapid deflagration or detonation.

Hot Wire Initiation in the Gas Phase. Under similar initial conditions of temperature and pressure, BASF (11), Union Carbide (1) and BICM (12) have obtained the following results.

	Initial Temperature $^{\circ}C$	Initial Pressure KN/m^2a	Initiation Energy J	Induction Period S	Limit mole % vinylacetylene
BASF	120	580	80	~1	40
Union Carbide	52	580	3.2	-	41-46
BICM	-	720	1000	-	87

The BICM limit was obtained using a very slow heating system, ie. 1000J applied to a wire over a period of about 30 secs, whereas the BASF and Union Carbide results were obtained by using an exploding wire system (BASF quote 60 milliseconds for their energy input). The BICM result cannot be compared directly with the other results, but does highlight the need for optimising time and geometry factors. The other results agree fairly well with those obtained in this work, but again illustrate the need for caution against trying to be too precise - results obtained reflect the cumulative effect of small changes in experimental conditions.

The difference in the limits found between the 0.5J and the 100J initiation can be explained if the Union Carbide's thermal work (1) is considered. They found that with a 46 mole % vinylacetylene mixture, an exotherm started at about $140^{\circ}C$ ie. $90^{\circ}C$ above the initial temperature used in this work. The specific heat of such a gas mixture is approximately 1.3J/g. Hence the 0.5J input of energy would raise approximately 0.04g (3 ml) of gas to the temperature where an exothermic reaction would start. Under static conditions this would be sufficient to initiate propagation; however in a dynamic system the energy from the exploding bridgewire would be dissipated by turbulance thus lowering the chances of initiating propagation. This would support the finding of a

lower limit when 100J were used and would also support the view that the initial temperature could be an important factor.

BASF also found an induction period measurable in seconds. This is most significant and proves conclusively that the mechanism of hot wire initiation is different from detonative initiation. The rises in temperature to above 500°C and pressure to values up to 13,000 KN/m²a in approximately 2 seconds can only be explained by a exothermic change propagating from the heated volume around the exploding wire. It is possible that this initial change is a polymerisation reaction, but because polymerisation reactions have ceiling temperatures which are well below the temperatures experienced in the explosion vessel, it must be concluded that a polymerisation quickly gives way to an exothermic decomposition reaction. This is substantiated by the thermal work carried out by Union Carbide. They also found that with 1,3-butadiene in the absence of vinylacetylene an exotherm starts at 150°C. However, under moderate conditions of temperature and pressure, 1,3-butadiene is not sufficiently energetic to undergo a propagating decomposition reaction; hence this exotherm is attributable to a polymerisation reaction. In a closed system, such a polymerisation would be accompanied by significant rises in temperature and pressure. Under the experimental conditions employed in this work, no such increases were observed at low concentrations of vinylacetylene. Therefore, it must be concluded that the initiation used does not induce a significant amount of polymerisation of the 1,3-butadiene.

In every experiment where there was an explosion, the bursting discs were removed cleanly indicating that the pressures acting on them were several times larger than those required to rupture them, ie. a pressure of several tens of thousand KN/m²a. As the response times of the pressure gauge and the recorder were in the 10 millisecond region, this final rise in pressure must have been very rapid, which suggests that the final stage of the decomposition was detonative in character.

Different terminal effects were observed by BASF who recorded final pressures of 5-9 times the initial pressures indicating that the decomposition was a simple deflagration without significant pressure piling. There was a deliberate difference in experimental procedure between the 2 studies. The aim in the present work was to have a liquid phase in equilibrium with the vapour phase. This liquid overload was calculated to be at least 50%. The thermal stability work done by Union Carbide (1) indicates that explosion is possible when the pressure in the system rises to between 5,000 and 13,000 KN/m²a. Hence with a liquid overload in the system, an increase in temperature will raise the pressure quickly because of volatilisation of the liquid phase. If the pressure exceeds 5,000 KN/m²a there is a strong likelihood of explosion. In all except 1 experiment where an explosion was recorded, the pressure in the vessel rose to between 5,000 and 13,000 KN/m²a before the bursting disc actuated.

Detonative Ignition. Classical detonation theory takes no account of the *physical state of the unreacted explosive.* For a condensed phase the low specific volume has a significant effect, largely due to the co-volume of the product gases being significant. The result is higher detonation velocities in the condensed phase (corresponding to lower detonation limits) than in the vapour phase. Experience supports this view, although it is difficult to quantify and the experimental data are limited.

Very approximate calculations suggest that the detonation temperatures of mixtures just above the limits for liquid and gas (41% and 62% respectively) are both in the region of 1,000 - 1,200°K. Although the classical equations are continuous functions and therefore do not define a lower limit, this region

of temperature seems from practical experience to be that required for reaction to proceed fast enough to support a detonation. Therefore the difference between the 2 limits seems to be rational. The difference in limits between detonative and hot wire ignition in the gas phase might suggest that lower values could be obtained in the liquid phase by exploding wire initiation. Experience with exploding wires in other liquids in this laboratory indicates that because of the marked quenching effects initiation is inhibited. The thermal stability results quoted by Union Carbide (1) show that another thermal mechanism leading to explosion is possible. They obtained exotherms leading to explosions at concentrations down to 17 mole % vinylacetylene under certain bulk temperature and pressure conditions.

Industrial Mixtures. (Table 3)

The charges for this series of experiments were made up from the industrial mixtures supplied by ICI by the addition of 1,3-butadiene. For this reason it was not possible to have strict control over the concentrations of the ethylacetylene and the 1,2-butadiene. On average, the charges for the gas phase and liquid phase experiments contained a combined 16-19 mole %, and 25-26 mole % respectively of these compounds. The explosion limits obtained may be summarised as follows:-

Phase	Initial Temperature ^{o}C	Initial Pressure KN/m^2a	Initiation	Limit Mole % Vinylacetylene
Gas	52	520	Detonator	52-54
Gas	52	520	0.5J	44-66
Gas	90	1030	100J	26-27
Liquid	25	-	Detonator	42

A comparison of the limits with those for the vinylacetylene/1,3-butadiene system shows that there is a lowering of the explosion limits caused by the presence of the 1,2-butadiene and the ethylacetylene. In the vapour phase, with 0.5J initiation this lowering is small and might be considered insignificant, but it must be noted that because of the presence of the other C4 materials the initial pressure was lower by 50-60 KN/m^2a. With detonative ignition in the vapour phase the explosion limits are 8-10% lower and again this difference is certainly under emphasized by the lower initial pressure.

At higher pressures and temperatures, the limit was markedly reduced to 26-27 mole % vinylacetylene. BASF found that a vinylacetylene/1,3-butadiene mixture containing approximately 7 mole % ethyl acetylene had an explosion limit between 24 and 30 mole % vinylacetylene at 120°C and 960 KN/m^2a with 80J hot wire ignition. Allowing for the differences in the initial conditions, these results are in reasonable agreement.

The induction periods that preceded the explosions in the vapour phase were similar in time and pressure development to those in the vinylacetylene/ 1,3-butadiene system.

The results suggest that ethylacetylene and 1,2-butadiene, which are both more energetic than 1,3-butadiene, play a small part in the reactions taking place during the induction period in the vapour phase and contribute significantly to the energy requirements for detonation.

Vinylacetylene/Acetonitrile Mixtures.(Table 4)

The explosion limit for mixtures of vinylacetylene/acetonitrile in the liquid phase was not well defined. However, it was not until the vinylacetylene concentration was above 58 mole % that the decomposition became significant. This is a high value when compared with the 40-42 mole % found for vinylacetylene/1,3-butadiene mixtures, indicating that acetonitrile has a significant phlegmatising effect.

A similar phlegmatising effect was observed some years ago in this laboratory when another explosive liquid was tested. Mixtures of this liquid with an inert solvent gave an explosion limit of 50 mole %. When mixed with aceto-nitrile, the explosion limit was 76 mole %. Initiation was with a No.8 detonator, and the samples were heavily confined. Since the mixture in this case had very low vapour pressures, it was possible to do the tests in a Ballistic Mortar which allowed the energy produced to be quantified. Thus, the results obtained were unequivocal. This evidence supports the thesis that the phlegmatising effect of acetonitrile is realistic.

CONCLUSIONS

The characteristics of the decomposition of C_4 unsaturated hydrocarbons containing vinylacetylene depend markedly on the type of initiation used.

In the vapour phase, there are 2 types of mechanisms for decomposition. With shock wave initiation the concentration of vinylacetylene necessary to support decomposition is approximately 60% and this decomposition is detonative in character. Below this concentration decomposition can be induced with much lower energies of initiation applied over longer periods of time. In these cases the decomposition is a deflagration which can turn into a detonation under the right conditions of temperature and pressure. Comparison of the results obtained with those of BASF clearly indicate that the presence of a liquid phase in equilibrium with the vapour phase is an important factor in determining whether decomposition initiated by exploding wire can become detonative in character.

In the liquid phase there are again 2 possible mechanisms for decomposition. With shock wave initiation, the limit is approximately 40 mole % vinylacetylene and the decomposition is detonative. Heating of the bulk material can lead to the onset of an exothermic reaction, which under very wide conditions of concentration can lead to explosive or detonative decomposition. Materials such as acetonitrile, which can act as an energy sink, have a remarkable phlegmatising effect, increasing the explosion limit for shock wave initiation from 40 to approximately 60 mole % vinylacetylene.

When considering safety features in industrial plant where vinylacetylene is involved, it is necessary to analyse carefully all the conditions that are likely to be encountered. Probably the most dangerous condition, and probably the condition in the Union Carbide plant immediately prior to the accident, is general heating of a liquid phase to a temperature where the exothermic reaction starts. Whether this exothermic reaction will lead to an explosion will depend to a large extent on reaction rates, heat transfer from the liquid, exhaustion of reactants, expansion space and venting. If the reaction is very fast, it is possible for the pressure to build up rapidly to a level where detonation can occur before venting takes place.

Decomposition in the vapour phase initiated by sparks will depend very largely on the pressure and vinylacetylene concentration. If plant is operated

such that the total pressure does not exceed 550 KN/m^{2}a and the vinylacetylene concentration is no greater than 30 mole % the possibility of decomposition initiated by sparks is extremely small.

ACKNOWLEDGEMENTS

REFERENCES

1. Buehler, J H, et al Chemical Engineering 1970, 77.
2. Jarvis, H C, Chemical Engineering Progress 1971, 67, 41.
3. Freeman, R H and McCready, M P, Chemical Engineering Progress, 1971, 67, 45.
4. Ikegami, T Rev. Phys Chem Japan 1963, 32, 13.
5. Ikegami, T   Ibid   1963, 33, 6.
6. Ikegami, T   Ibid   1963, 33, 15.
7. Ikegami, T   Ibid   1963, 33, 65.
8. Mushii, R Ya., and Glikin, M A Vestnik Tekln. i Ekonom Issled Gos Kem Khim i Neft Prom pri Gosplane SSSR 1963, 7, 28.
9. Kitagawa, T, Kitagawa, C and Nishimura, T., Kogyo Kagaka Zasshi 1964, 67, 1570.
10. Nelson, H H, Combustion Institute, 6th Symposium on Combustion 1956, 823.
11. BASF Laboratories. Private Communication.
12. Carver, F W S, Smith, C M and Webster, G A, I Chem E Symposium Series No.33 1972, 44.
13. BICM Laboratories. Private Communication.

TABLE 1. Ignition of Vinylacetylene/1,3-butadiene in the vapour phase.

Mole % VA	Initiation	Vessel Conditions		Observations				
		$T_1 °C$	P_1 $KN/m^2 a$	S	BD	$T_2 °C$	P_2 $KN/m^2 a$	t.sec
56	Detonator	52	518	ND	NF	–	–	–
58	Detonator	51	551	ND	NF	–	–	–
61	Detonator	52	586	ND	NF	–	–	–
62	Detonator	52	551	ND	NF	–	–	–
62	Detonator	51	551	D	F	–	–	0
64	Detonator	52	551	D	F	–	–	0
36.3	100J	53	565	ND	NF	–	–	–
37.7	100J	52	572	ND	NF	–	–	–
39.3	100J	52	565	ND	NF	–	–	–
41.3	100J	53	586	ND	NF	–	–	–
41.3	100J	52	565	D	NF	–	–	–
42.0	100J	51	600	D	F	>500	5720	>2
43.6	100J	51	572	D	F	>500	5380	>2
45.1	0.5J	52	551	ND	NF	–	–	–
45.3	0.5J	51	565	ND	NF	–	–	–
46.9	0.5J	52	600	ND	NF	–	–	–
47.3	0.5J	51	572	D	F	–	2930	2.2
49.4	0.5J	52	572	D	F	960	*9170	2.7
51.0	0.5J	52	579	D	F	–	4600	2.1
53.7	0.5J	52	572	D	F	960	*9170	2.3
57.8	0.5J	52	600	D	F	710	*9930	2.0

VA = Vinylacetylene; T_1 = Initial temperature; P_1 = Initial Pressure;
T_2 = Maximum temperature recorded; P_2 = Maximum pressure recorded;
S denotes decompositon (D) or no Decomposition (ND)
BD denotes where bursting disc failed (F) or did not fail (NF);
t = Time between initiation and failure of the bursting disc.

The charge weight used varied between 60 and 70 g.

Those experiments marked * had bursting discs designed to fail at
18,200 $KN/m^2 a$; in all other experiments the bursting discs were
designed to fail at 8,300 $KN/m^2 a$.

TABLE 2. Ignition of Vinylacetylene/C_4 hydrocarbon mixture in the vapour phase.

Composition Mole %				Vessel Conditions		Initiation	Observations				
VA	1,3-BD	1,2-BD	EA	T_1 °C	P_1 KN/m²a		S	BD	T_2 °C	P_2 KN/m²a	t secs
49	33.4	9.2	8.4	51	517	Detonator	ND	NF	–	–	–
51.1	30.2	10.1	8.6	53	503	Detonator	ND	NF	–	–	–
51.3	31.3	9.7	7.7	53	497	Detonator	ND	NF	–	–	–
53.9	28.9	9.4	7.8	52	483	Detonator	D	F	–	–	–
54.4	32.2	7.3	6.1	52	524	Detonator	D	F	–	–	–
56.7	26.8	9.0	6.1	52	524	Detonator	D	F	–	–	–
58.7	25.5	8.2	7.6	52	517	Detonator	D	F	–	–	–
62.7	21.1	8.8	7.4	52	483	Detonator	D	F	–	–	–
36.4	46.2	9.3	8.0	52	517	0.5J	ND	NF	–	–	–
42.5	39.8	9.7	8.0	52	470	0.5J	ND	NF	–	–	–
42.9	37.7	10.7	8.7	52	510	0.5J	ND	NF	–	–	–
44.3	40.2	8.6	6.8	50	503	0.5J	D	F	>500	6000	2.3
44.5	37.8	9.6	8.0	52	524	0.5J	ND	NF	–	–	–
45.9	36.4	10.1	8.2	52	517	0.5J	ND	NF	–	–	–
46.3	35.2	10.0	8.5	51	517	0.5J	D	F	>500	2960	1.8
47.5	34.6	9.8	8.1	51	524	0.5J	D	F	>500	6420	2.1
48.1	32.6	10.7	8.6	52	531	0.5J	D	F	>500	6280	2.6
25.9	61.3	7.1	5.7	90	1020	100J	ND	*NF	–	–	–
26.0	58.7	7.9	7.4	90	1035	100J	D	*F	–	12,900	5.2
26.9	54.2	9.5	9.4	90	1035	100J	ND	*NF	–	–	–
27.6	56.5	8.5	7.4	87	1030	100J	D	*F	–	12,900	4.5
28.1	58.8	7.3	5.8	90	1035	100J	D	*F	1160	12,900	3.0
37.1	43.2	11.0	11.0	90	1020	100J	D	*F	1060	13,300	1.5

VA = Vinylacetylene; 1,3-BD = 1,3-butadiene; 1,2-BD = 1,2-butadiene;
EA = Ethylacetylene; T_1 = Initial temperature; P_1 = Initial pressure;
T_2 = Maximum temperature recorded; P_2 = Maximum pressure recorded;
S denotes decomposition (D) or no decomposition (ND);
BD denotes failure of bursting disc (F) or non failure of bursting disc (NF);
t = Time between initiation and failure of bursting disc.

In experiments other than those marked with * the charge weight was 60–70 g, and the bursting disc was designed to fail at 8,300 KN/m²a.

Those marked * had a charge weight of 90–100 g, and a bursting disc designed to fail at 18,200 KN/m²a.

TABLE 3. Vinylacetylene/C_4 mixtures in the liquid phase; initiation by No.8 Aluminium sheathed flat based detonators.

Charge Wt g	Composition Mole %				Vessel Temp °C	Observations
	VA	1,3BD	1,2BD	EA		
41.9	38	62	–	–	28	ND
39.1	40	60	–	–	25	ND
46.1	41	59	–	–	26	ND
27.1	41	59	–	–	26	ND
42	41	59	–	–	25	ND
36.3	41	59	–	–	26	ND
42.1	42	58	–	–	26	D
39	42	58	–	–	25	D
20	42	58	–	–	25	ND
26	43	57	–	–	25	ND
46.7	40	60	–	–	52	D
32.3	40	60	–	–	52	ND
26.1	40	60	–	–	52	ND
43.0	41	59	–	–	52	ND
29.3	42	58	–	–	52	D
25.8	42	58	–	–	52	D
25.6	43	57	–	–	52	D
33.8	35.2	41.8	–	–	25	ND
31.1	38.9	35.7	14.3	11.1	25	ND
29.1	41.7	30.8	15.8	11.7	25	ND
30.3	42.3	30.4	15.4	11.6	25	Decomp

VA = Vinylacetylene;   1,3BD = 1,3-butadiene;   1,2BD = 1,2-butadiene
EA = Ethylacetylene;   ND = No decomposition;   D = Decomposition

TABLE 4. Vinylacetylene/Acetonitrile Mixtures in the liquid phase: initiation by No.8 Aluminium sheathed flat-based detonators.

Charge Wt g	Mole % VA	Observations
30.9	46.6	No Decomposition
31.1	46.6	No Decomposition
30.5	47.6	Slight Decomposition
30.0	54.8	Slight Decomposition
27.7	57.8	Slight Decomposition
39.2	60.0	Decomposition. Weak Explosion[1] as contents vented
29.1	60.0	Decomposition. Weak Explosion[1] as contents vented
24.0	62.2	Decomposition. Weak Explosion[1] as contents vented
31.4	62.2	Decomposition. Weak Explosion[1] as contents vented
29.3	63.7	Decomposition. Explosion as[2] contents vented
29.0	63.7	Decomposition. Explosion as[2] contents vented
29.7	67.6	Decomposition. Explosion as[2] contents vented
29.3	67.6	Decomposition. Explosion as[2] contents vented

1. Contents vented through detonator holder

2. Detonator plug blown out

FIG.I. VESSEL USED FOR VAPOUR PHASE EXPERIMENTS

A.-SAMPLE TAKE OFF.
B-INLET.
C-THERMOCOUPLE.
D-PRESSURE TAKE OFF.
E-STRAIN GAUGE.

CAPACITY OF VESSEL 2·6LITRES.

38MM. DIA.
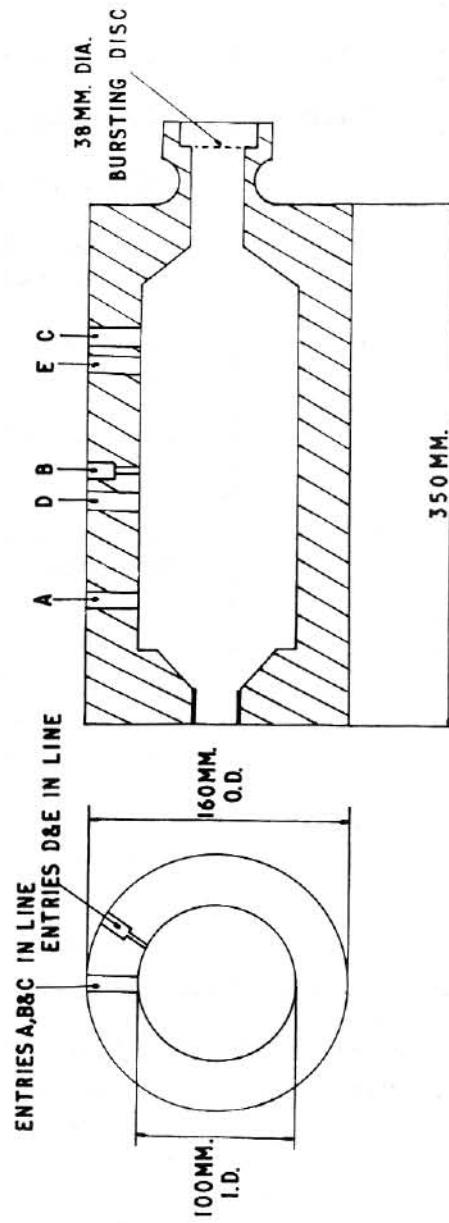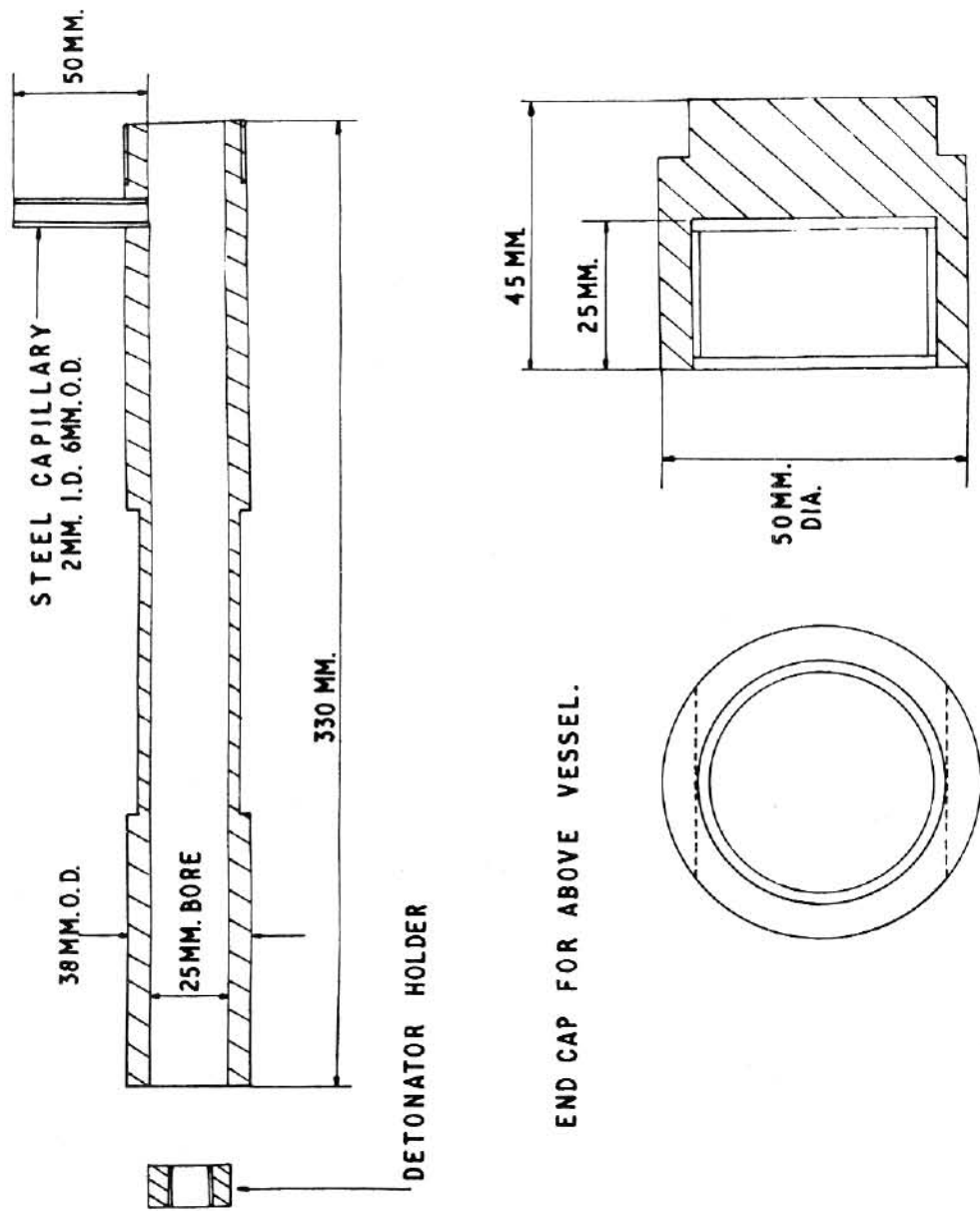BURSTING DISC

350MM.

160MM. O.D.

100MM. I.D.

ENTRIES A,B&C IN LINE
ENTRIES D&E IN LINE

FIG. 2. VESSEL USED FOR LIQUID PHASE EXPERIMENTS

50 MM.

STEEL CAPILLARY
2MM. I.D. 6MM.O.D.

330 MM.

38MM.O.D.

25MM. BORE

DETONATOR HOLDER

45 MM

25 MM.

50 MM.
DIA.

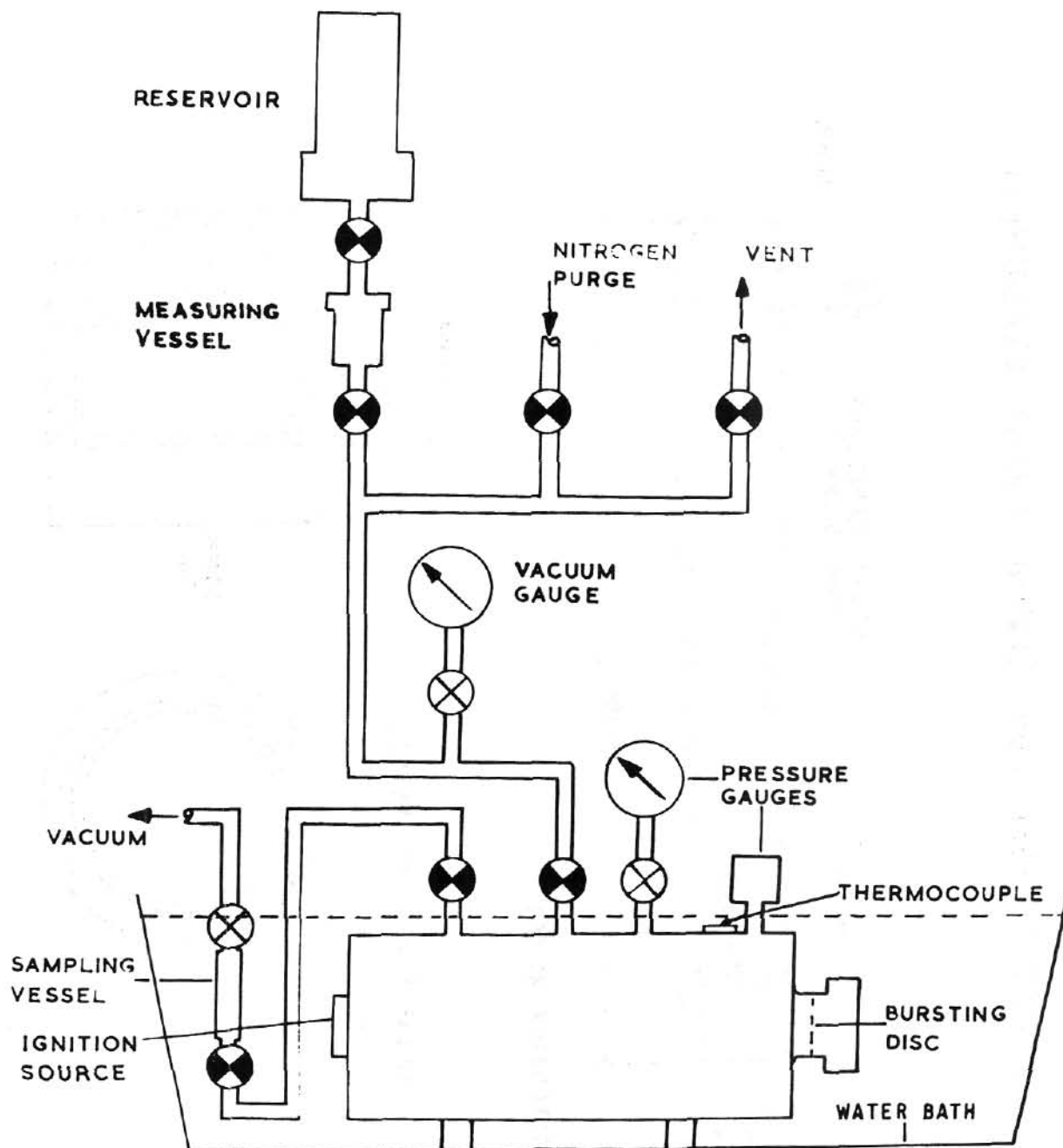END CAP FOR ABOVE VESSEL.

113

FIG.3. EXPERIMENTAL ARRANGEMENT FOR FILLING VAPOUR
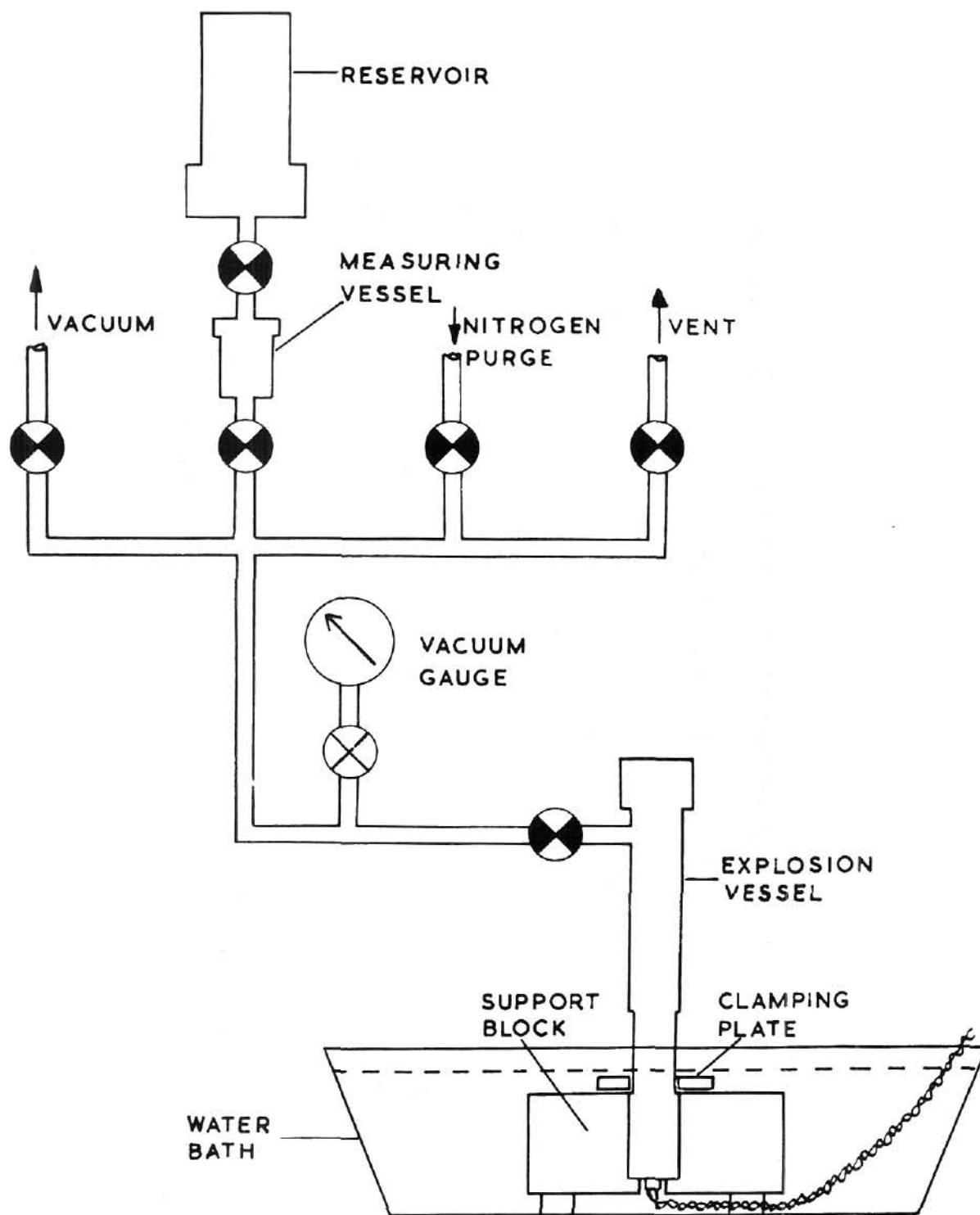EXPLOSION VESSEL

114

FIG.4. EXPERIMENTAL ARRANGEMENT FOR FILLING LIQUID
EXPLOSION VESSELS

115

FIG.5. PRESSURE & TEMPERATURE VS. TIME GRAPHS FOR INDUSTRIAL GAS MIXTURE WITH 100 JOULE INITIATION.

116