

THE EXPLOSIVE DECOMPOSITION OF ETHYLENE OXIDE VAPOUR UNDER PRESSURE

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SUMMARY

To assess the hazards involved in the handling of ethylene oxide vapour in plant where a source of ignition may exist, an investigation has been made of the explosive decomposition of this material at 125°C and pressures up to 155 lb/in² abs and its mechanism considered. The igniting source employed consisted of a length of 31 s.w.g. Nichrome wire which was fused electrically. It is shown that the explosion is capable of suppression by inert diluents and the use of nitrogen in this connection has been particularly investigated. Less detailed observations have been made with ethylene, propane and butane as diluents. It was found that propylene oxide did not undergo explosive decomposition at 125°C and pressures up to 165 lb/in² abs.

Introduction

Ethylene oxide first assumed some commercial importance as a fumigant for the control of insect pests in foodstuffs. During the last twenty years, however, its widespread use as a chemical intermediate in the production of ethylene glycol and ethylene glycol derivatives has raised its status to that of a "heavy organic chemical". The rapid expansion in its use in the U.S.A. may be judged by an increase in the estimated consumption from 108 million pounds in 1939 to 354 million pounds in 1949;¹ during the last decade, estimated production has jumped to 1300 million pounds.² By the end of 1960 it is estimated that production capacity in the United Kingdom will exceed 100 million pounds. If ethylene oxide is put to the same uses as in 1957, then 40% of the total production will be required for the manufacture of ethylene glycol; the processing of solvents for the paint industry will account for 20% and that of liquid synthetic detergents for a further 15%.

At atmospheric pressure all mixtures of ethylene oxide in air containing more than 3% ethylene oxide are capable of being ignited. Following the occurrence of several explosions during fumigations, consideration was given some years ago to reducing the flammability of ethylene oxide in air. Early studies of its physiological properties had shown that its pesticidal effect is promoted by the presence of carbon dioxide which increases the respiration rate of the insect. For this reason, it was the custom to introduce 10% carbon dioxide into commercial ethylene oxide for use as a fumigant, a practice which also raised the vapour pressure to a convenient level for discharge from the cylinder. It is not surprising, therefore, that carbon dioxide was early considered for the purpose of suppressing the flammability of ethylene oxide. Jones and Kennedy⁸ determined the effect of carbon dioxide on the limits of its flammability in air; their results were later confirmed by other investigators^{9,10} using different experimental conditions. All possible mixtures of ethylene oxide in air can be made non-flammable at atmospheric temperature and pressure by adding at least 7-15 volumes of carbon dioxide to each volume of ethylene oxide present.¹¹

In the absence of air, ethylene oxide is capable of exothermic decomposition and it has seen some use as a mono-

propellant in rocket motors. The liquid is stable when pure^{4,5} but at atmospheric temperature an exothermic polycondensation reaction in the liquid phase may be catalysed by impurities such as caustic soda.⁶ The heat released during this process may cause the vapour pressure of the unreacted material to exceed the bursting pressure of a closed vessel.

The spontaneous decomposition temperature of pure ethylene oxide vapour at atmospheric pressure is reported^{1,2} to be 571°C and it has been shown⁷ that if a local source of ignition, such as a hot wire, is applied to ethylene oxide vapour, a decomposition reaction, accompanied by flame, may propagate from it and throughout the vapour if the latter is at a pressure greater than approximately atmospheric. The precise pressure limit for flame propagation which is observed depends upon the energy of the igniting source and the conditions of confinement.

The use of inert diluents to suppress the explosive decomposition of ethylene oxide in the absence of air was first investigated by Hess and Tilton.¹² There is some doubt as to the exact conditions of temperature and pressure under which they carried out their investigation but it is thought that they worked with a constant partial pressure of ethylene oxide of 45 lb/in² abs at a temperature of 40.45°C. In presenting their results, however, they assumed that the percentages of inert diluents needed to suppress the explosive decomposition of ethylene oxide vapour at partial pressures of 15.75 lb/in² abs and temperatures from 10-60°C were constant.

The increasing industrial use of ethylene oxide at higher temperatures and pressures has necessitated an investigation of the effect of these conditions on the amount of diluent needed to suppress explosive decomposition. In this connection the use of nitrogen has been investigated in some detail because it is readily available in large quantities. Less detailed observations have been made on the hydrocarbons, ethylene, propane, and butane.

Experimental

Apparatus

The explosion vessel used in this investigation, shown diagrammatically in Fig. 1, had an internal diameter of 4.5 in. and an internal volume of 148.9 in³. It was designed for a maximum dynamic pressure of 1500 lb/in² g. To reduce any tendency towards catalytic decomposition of the ethylene

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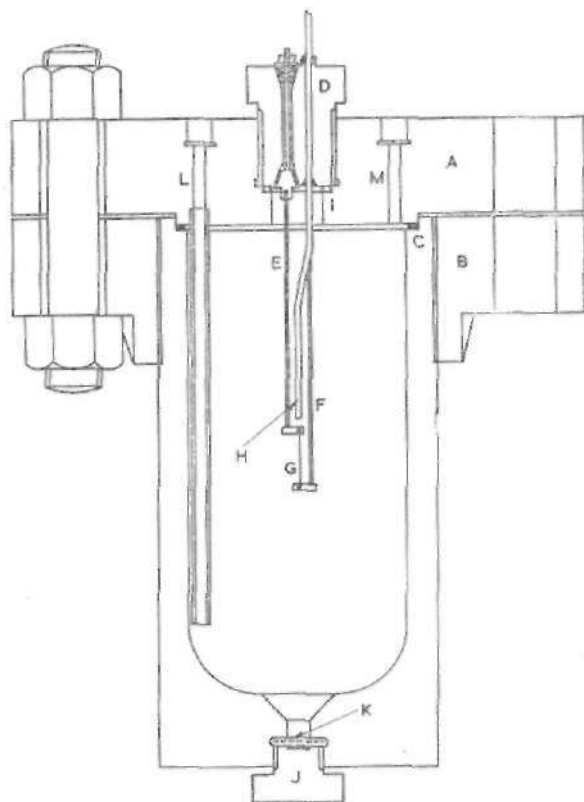


Fig. 1.—Experimental pressure vessel

oxide vapour on the walls, all those parts of the vessel coming into contact with the vapour were made of austenitic stainless steel (En specification 58B). No copper, silver, or other acetylide-forming metals were used in the construction of the vessel and its ancillary equipment in order to prevent the possible formation of acetylides which, if detonated, could have initiated prematurely the explosive decomposition of ethylene oxide.

The end cover, A, was attached to the screwed flange, B, by eight high-tensile steel nuts and bolts; a semi-confined fiat gasket, C, machined from fully annealed nickel, formed the seal between the cover and the end of the vessel. The firing plug, D, was provided with two electrodes, one of which, E, was electrically insulated from the plug by two cone-shaped Fluon bushes, while the other, F, served as an earth return. The ignition source, G, which consisted of a straight piece of 31 s.w.g. Nichrome wire 0.8 in. long clamped between the electrodes, was located near the centre of the vessel; the end of a stainless steel sheathed thermocouple, H, which was welded into the firing plug was located near the ignition source. A hollow pressure-filled nickel joint ring, I, was used to obturate the firing plug so that the pressure-tight seal could be remade frequently without the use of excessive force. Provision was made to evacuate and fill the vessel through the two pipe inlets, M and L, the latter being provided with a pipe extension inside the vessel designed to promote mixing when an inert gas was added to the ethylene oxide.

The dynamic pressure measurements were made using two condenser-type pressure gauges, J. These gauges, one of which had a pressure range of 0-600 lb/in² g, and the other 0-1500 lb/in² g, were provided with flush, stainless steel diaphragms. The gauge in use was accommodated in a

screwed recess at the end of the vessel, the seal being made on a nickel washer located between the body of the gauge and the outside surface of the vessel.

When in use each gauge formed part of the tuned circuit of an oscillator; the radio frequency signal resulting from a change in capacitance of the gauge was fed to a frequency modulated pre-amplifier the output voltage of which was directly proportional to the change in capacitance and hence directly proportional to the pressure change on the diaphragm of the gauge. The output signal from the pre-amplifier, after suitable amplification, was displayed on the main cathode ray tube of an oscillograph. Electrical pulses of 0.1 s duration produced by a time marker, consisting of a tuning fork controlled vibrator circuit, were applied to a small marker tube. A permanent pressure-time record of the explosion, such as that shown in Fig. 3, was obtained by photographing both cathode ray tubes simultaneously with a rotating drum camera. The mark A on the record shows the time at which the wire was caused to fuse.

Each gauge, when screwed into position in the explosion vessel and maintained at the required operating temperature, was statically calibrated over the whole of its working range. The calibration, using nitrogen as the pressure-transmitting fluid, was made against a Bourdon-tube testing gauge which had been previously calibrated against a dead-weight pressure tester. To obviate the tightening-in effect caused by the distortion of the body of the condenser gauge when it was screwed into the vessel against the sealing gasket, it was necessary to recalibrate the gauge each time it was reseated in the vessel. In order to reduce the error in the pressure measurement caused by the flame front impinging on the diaphragm the gauge was protected by a piece of 200 mesh stainless steel gauze, K (see Fig. 1) which was fixed 0.125 in. in front of the diaphragm.

The vessel was supported at the centre of an enclosed electrically-heated oven which could be adjusted and controlled at any temperature from 25-200°C. Provision was made for the firing plug and pressure gauge to be withdrawn and replaced in the vessel as required, without having to remove the oven. Four thermocouples fixed to various points on the vessel enabled the temperature distribution over the outside surface of the vessel to be measured. It was found that when thermal equilibrium had been established with the contents of the vessel at 125°C the difference between the temperature at any point on the outside surface of the vessel and that at the centre did not exceed $\pm 2^\circ\text{C}$.

Fig. 2 shows a flow diagram of the ancillary equipment used to charge the vessel with ethylene oxide vapour and inert diluent. As in the case of the explosion vessel the pipe lines, valves, and all those items of equipment which came into contact with the ethylene oxide vapour were made from austenitic stainless steel.

Liquid ethylene oxide was stored under its own vapour in the feed-vessel, A, which could be refilled through a screwed cap. This vessel, which had an internal volume of 23.5 in³, was designed to withstand a working pressure of 200 lb/in² g; it was protected by a bursting disc, B, rated to rupture at 250 lb/in² g.

Procedure

The detailed procedure for filling the explosion vessel with a mixture of ethylene oxide and inert diluent of known composition depended on the total pressure required and the vapour pressure of the inert diluent in the storage container. The procedure described here was that applied to an inert

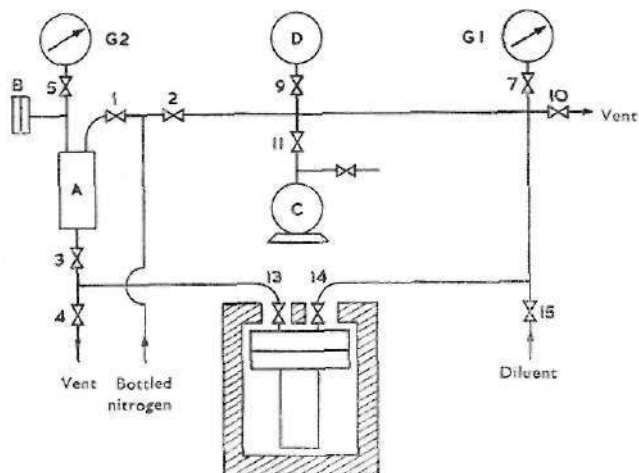


Fig. 2.—Flow diagram of ancillary equipment used to charge vessel with ethylene oxide vapour and inert diluent

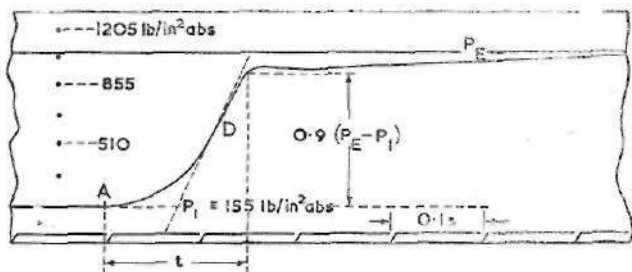


Fig. 3.—Pressure-time record of the decomposition of ethylene oxide at an initial pressure of 155 lb/in² abs and temperature of 125°C

diluent, such as ethylene, bottled in the form of a compressed gas.

After the explosion vessel had attained the correct temperature, usually 125°C, all valves except Nos. 7, 9, 11, 13, and 14 were closed and the vessel was evacuated using a rotary pump until the pressure recorded by the vacuum manometer, D, with valve 11 closed, was less than 1 mm mercury. Oxygen-free nitrogen was then admitted through valve 2 until a small pressure was registered by the compound Bourdon-tube gauge G.1 after which valve 2 was closed and the vessel re-evacuated. Valve 14 was then closed and valve 3 opened to allow ethylene oxide to be drawn slowly into the explosion vessel where it quickly vaporised until the vapour pressure in the explosion vessel was equal to that in the feed vessel. Oxygen-free nitrogen was then slowly admitted to the feed vessel via valve 1 and used to force more ethylene oxide into the explosion vessel until the required pressure of the ethylene oxide vapour as registered by the Bourdon tube gauge, G.2, had been attained. When equilibrium had been established valves 1 and 13 were closed and the remaining ethylene oxide in the feed bottle and pipe line was removed by a wet vacuum pump through valve 4. The inert diluent was admitted through valve 15, valves 9 and 11 being closed, until the pressure recorded by the compound Bourdon-tube gauge, G.1, was slightly less than the total pressure required in the explosion vessel. Valve 14 was opened and inert gas admitted to the vessel until the required total pressure was obtained. Valves 15 and 4 were then closed and the inert

diluent in the pipe line was withdrawn through valve 10 using the wet vacuum pump.

After allowing about half an hour for the ethylene oxide and diluent to mix thoroughly the igniting wire was fused and the pressure-time trace photographed. When the products had cooled to 125°C the pressure in the vessel was measured using gauge G.1 after which the vessel was evacuated by the wet vacuum pump. In order to obtain consistent results for the dynamic pressure measurements it was found necessary to remove periodically the carbon deposited on the inside surface of the vessel as a result of the decomposition reaction.

Experimental Results

A preliminary series of experiments was made to ensure that the energy dissipated by the ignition source was adequate. No attempt was made in these experiments to measure the electrical energies dissipated; instead, Nichrome wires (80% Ni 20% Cr) of various diameters and each 0.8 in. long were caused to fuse by using an alternating current of 10A at 240 volts. In Fig. 4, the percentage of nitrogen necessary to suppress the explosion of ethylene oxide at a partial pressure of 85 lb/in² abs and 125°C is shown as a function of the gauge and the cross-sectional area of the wire. It may be seen from this figure that provided the diameter of the Nichrome wire is greater than 34 s.w.g. the limit of explosibility of ethylene oxide in nitrogen is independent of the diameter to within the mean experimental error of the measurements (estimated to be $\pm 1.5\%$). The source of ignition used for all subsequent experiments consisted of a straight piece of 31 s.w.g. Nichrome wire 0.8 in. long, the fusion temperature of which was taken as 1400°C.

Commercially available ethylene oxide and inert diluents were used without further purification; the sources of supply and the probable impurities are given in the Appendix.

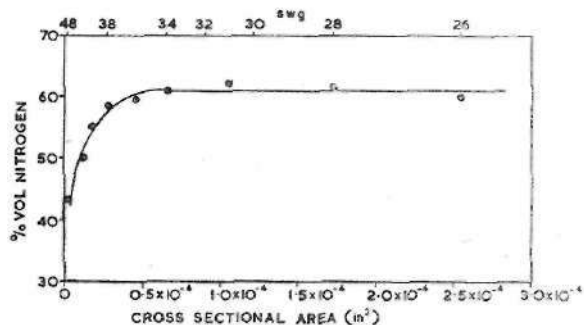


Fig. 4.—Percentage of nitrogen necessary to suppress decomposition of ethylene oxide at a partial pressure of 85 lb/in² abs and at 125°C shown as a function of the cross-sectional area of the igniting wire

Explosive decomposition of ethylene oxide vapour

The ratio of the maximum explosion pressure, P_E , to the initial pressure of ethylene oxide vapour, P_i , and the ratio of the final pressure of the products of combustion, P_F , to P_i are both plotted against P_i in Fig. 5. P_F and P_i were measured at 125°C and the ratios were calculated on the basis of the absolute pressures. Although the ratio P_E/P_i increases to about 6.4 when the initial pressure of ethylene oxide vapour is 155 lb/in² abs, the rate of the pressure rise was comparatively slow. Fig. 3 shows the pressure-time record for the explosion of pure ethylene oxide vapour at 155 lb/in²

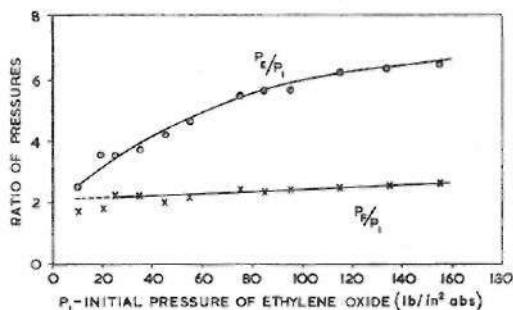


Fig. 5.—The maximum explosion pressure, P_E, and the pressure of decomposition products, P_F, at 125°C as a function of the initial pressure of ethylene oxide, P₁ at 125°C

abs. The maximum rate of increase of pressure (dP/dt)_{max} which occurs at D is only 1.2 × 10⁴ lb/in² s. In Fig. 6, values of (dP/dt)_{max} and the time taken, t, for the pressure to reach 90% of its maximum value are plotted against the initial pressure of ethylene oxide vapour.

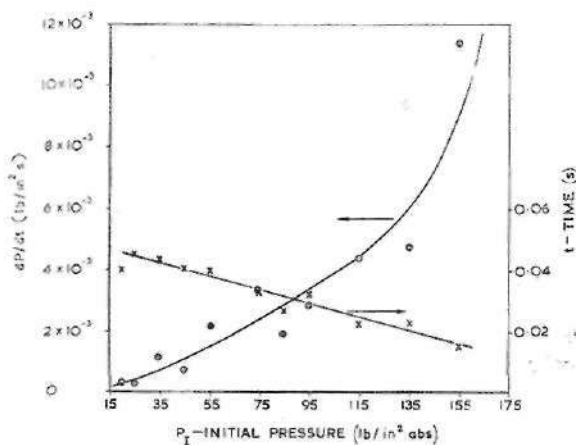


Fig. 6.—The maximum rate of pressure increase, dP/dt, and the time taken to develop 90% of the maximum explosion pressure as a function of the initial pressure of ethylene oxide

A chromatographic analysis of the gaseous decomposition products of ethylene oxide at initial pressures of 45 and 135 lb/in² abs was made using an apparatus incorporating a multicell thermal conductivity detector developed by Boreham and Marhoff¹⁴. The results of these analyses given in Table I show that at the higher pressure there is a marked reduction in the proportion of undecomposed ethylene oxide.

TABLE I.—Analysis of the Gaseous Products of Combustion
Composition of gas before ignition

Partial pressure C ₂ H ₄ O (lb/in ² abs)	45	135	85	85
Partial pressure N ₂ (lb/in ² abs)	—	—	16	55
Vol % N ₂	—	—	16	39
Analysis of gaseous products (Vol %)				
H ₂	15.1	16.1	15.3	7.2
CO	44.6	47.0	42.0	34.3
O ₂	0.0	0.2	0.2	0.2
N ₂	0.0	0.0	8.2	24.3
CH ₄	29.6	35.3	29.9	27.3
C ₂ H ₆	1.2	1.0	1.0	0.9
CO ₂	0.2	0.3	0.2	0.3
C ₂ H ₄	1.1	0.0	0.2	0.3
C ₂ H ₄ O (by difference)	8.2	0.1	3.0	5.2

The explosibility of propylene oxide

It appears from thermochemical considerations that propylene oxide is also capable of undergoing exothermic decomposition. It is possible, therefore, that at sufficiently high temperatures or pressures the vapour may become explosible on the application of a suitable source of ignition.

Using the same apparatus and procedure as for ethylene oxide, propylene oxide vapour at 125°C and at pressures up to 165 lb/in² abs was subjected to the standard ignition source (fusion of 31 s.w.g. Nichrome wire), but no sign of flame propagation as indicated by pressure rise was observed. It was concluded that propylene oxide vapour is not explosible at or below 165 lb/in² abs at 125°C.

Effect of inert diluents

In Fig. 7 the percentages by volume of nitrogen, ethylene propane, and butane necessary to suppress the explosive decomposition of ethylene oxide vapour at 125°C are plotted against the partial pressure of ethylene oxide in the gas mixture before ignition. These percentages were calculated on the assumption that all the gases obey the perfect gas laws over the range of pressure and temperature investigated.

It may be seen from this figure that whereas the percentage of diluent to suppress the explosibility of ethylene oxide increases with the partial pressure of the oxide vapour in nitrogen and in ethylene, in propane and butane the percentage appears to be constant over the limited range of pressures investigated. If 3% by volume of oxygen is added to the ethylene oxide vapour the requisite proportion of nitrogen at a partial pressure of ethylene oxide of 85 lb/in² abs is increased from 61.4 to 67.4%. Thus, had pure nitrogen been used for the experiments the values would have been only 0.3% lower.

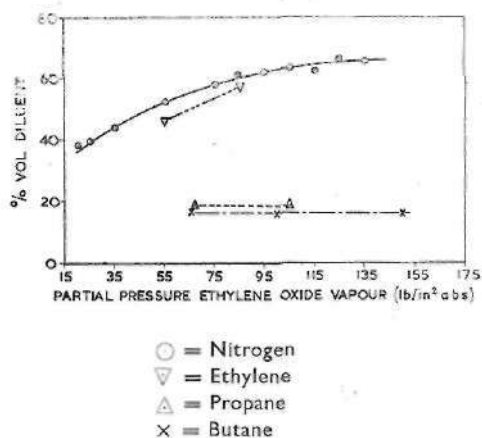


Fig. 7.—The percentage of various diluents necessary to suppress the decomposition of ethylene oxide vapour at 125°C as a function of the partial pressure of ethylene oxide

Over the temperature range 89-184.5°C the percentage of nitrogen needed to suppress the explosive decomposition of ethylene oxide under a partial pressure of 85 lb/in² abs was constant to within ±2%. Thus, within this range temperature appears to have very little effect on the limit of explosibility of ethylene oxide in nitrogen and, if it is assumed that this is true at a temperature of 60°C, then a comparison may be made between the results obtained by Hess and Tilton¹² and those from this investigation. Whereas the results given by Hess and Tilton indicate that 25% nitrogen will suppress

the explosive decomposition of ethylene oxide at a partial pressure of 75 lb/in² abs, those obtained in this investigation suggest that 58% nitrogen is necessary. If Hess and Tilton are correct in assuming that the partial pressure of the ethylene oxide vapour does not affect the proportion of nitrogen necessary to suppress the decomposition, then the discrepancy between the results indicates that much more inert diluent is needed to suppress the decomposition when it is initiated by a fused Nichrome wire, as in the present work, than when it is initiated by a heated platinum coil.

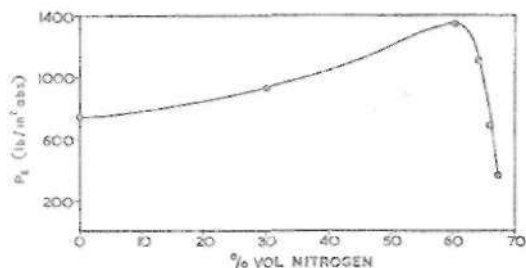


Fig. 8.—The pressures developed on ignition of mixtures of nitrogen and ethylene oxide in which the partial pressure of ethylene oxide is 125 lb/in² abs

In Fig. 8 the explosion pressures developed on igniting various mixtures of nitrogen and ethylene oxide at a constant partial pressure of ethylene oxide of 125 lb/in² abs are shown as a function of the percentage of nitrogen in the mixture. It may be seen that whereas the explosion pressure of pure ethylene oxide at a pressure of 125 lb/in² abs is 760 lb/in² abs that of a mixture containing 60% nitrogen is 1350 lb/in² abs. Thus for any application in which an inert diluent is required to suppress the decomposition of ethylene oxide it is important to ensure that *insufficient* diluent is *not* used. With ethylene oxide at a partial pressure of 125 lb/in² abs at least 67% of nitrogen is needed to suppress explosive decomposition at 125°C.

Table I gives the analysis of the gaseous products of decomposition from two experiments in which ethylene oxide at a partial pressure of 85 lb/in² abs was diluted with different amounts of nitrogen. These results show that the percentage of ethylene oxide in the decomposition products increases as the percentage of nitrogen in the mixture before ignition increases. At the limit, 61% nitrogen, all the ethylene oxide will remain undecomposed.

Effects of the internal size and shape of the vessel

The explosion vessel shown in Fig. 1 had an internal volume to surface area ratio, V/A , of 0.935 in³/in² and an internal volume of 148.9 in³. In order to investigate the effect of the size and shape of the container on the explosive decomposition of ethylene oxide two stainless steel, open-ended liners were provided, each of which fitted tightly into the explosion vessel. The first liner, which halved the internal volume of the vessel, was designed so that the ratio of the internal overall length to diameter, $L/D = 2.25$, was the same as that of the original vessel. Although the internal shape of the explosion enclosure within this liner corresponded to that of the original vessel, the ratio V/A was 0.730 in³/in². The second liner was designed to decrease the ratio V/A to 0.238 in³/in²; this necessitated reducing the internal volume to 8.0 in³ and increasing the ratio L/D to

6.77. The effects of changing the size and shape of the explosion enclosure on the pressures developed during the decomposition of ethylene oxide and on the limit of explosibility of ethylene oxide in nitrogen are summarised in Table II. It would appear from the low values of PF/PI that decomposition may not have been complete in the case of the vessel having the smallest volume.

TABLE II.—The Effect of the Size and Shape of the Container on the Explosive Decomposition of Ethylene Oxide

	Vessel	Liner I	Liner II
Internal volume V (in ³)	148.9	79.7	8.00
Ratio V/A (in ³ /in ²)	0.935	0.730	0.238
Ratio L/D	2.25	2.25	6.76

Explosion of (CH₂)₂O vapour at pressure P_1

P_1 (lb/in ² abs)	Vessel			Liner I			Liner II		
	$\frac{P_E}{P_1}$	$\frac{P_F}{P_1}$	t (s)	$\frac{P_E}{P_1}$	$\frac{P_F}{P_1}$	t (s)	$\frac{P_E}{P_1}$	$\frac{P_F}{P_1}$	t (s)
55	4.8	2.19	0.40	4.6	2.18	0.40	2.9	2.10	0.17
85	5.5	2.36	0.27	5.1	2.34	0.30	3.5	2.06	0.13
125	6.2	2.53	0.21	5.8	2.48	0.17	—	—	—

Explosive for (CH₂)₂O vapour at partial pressure P_1 in N₂

P_1 (lb/in ² abs)	Vessel	Liner I	Liner II
	Percentage nitrogen by volume		
55	52.3	56.2	—
85	61.4	61.4	65.4
125	66.5	70.7	—

* t = time to develop 90% of the maximum explosion pressure P_E .

In Fig. 9 the values of the ratio PE/PI obtained with the various liners are compared with those obtained by Hess and Tilton¹² using vessels which covered a wider range of ratios of volume to surface area.

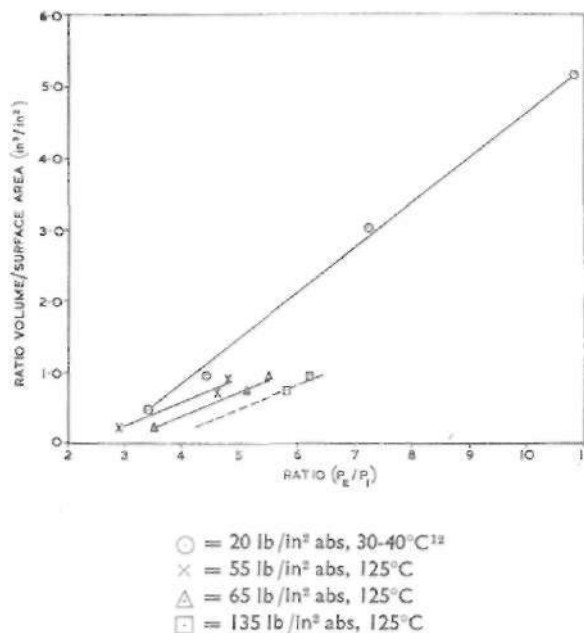


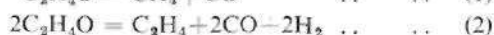
Fig. 9.—Effect of the ratio of volume to surface area on the explosion pressures developed during the decomposition of pure ethylene oxide

Discussion

This investigation confirms that the observed limit for flame propagation in a mixture of ethylene oxide vapour and inert diluent depends on the energy of the igniting source. Although it was calculated, assuming that no heat was lost, that the energy needed to fuse the whole length of the standard 31 s.w.g. Nichrome wire was about 10 joules, only a small proportion of this would be transferred to the gas during the ignition process. Fig. 4 suggests that when the energy dissipated in the igniting source exceeds a certain critical value the explosive limit is independent of the size of the source. Thus the use of a source whose energy exceeds this critical value should ensure that the results are unaffected by minor variations in power input. It is believed that results similar to those in Fig. 4 would have been obtained using a low energy igniting source provided the energy was released very quickly as in a condenser spark.

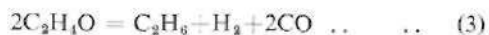
The increase in the values of the ratios P_E/P_1 and P_F/P_1 as the initial pressure increases may be partly ascribed to the effect of pressure on the amount of ethylene oxide undergoing decomposition. The analyses in Table I showed that at an initial pressure of 45 lb/in² abs, 15.4% of the ethylene oxide remained undecomposed while at a pressure of 135 lb/in² abs the amount was less than 0.2%.

Although the non-explosive thermal decomposition of ethylene oxide vapour has been studied by a number of investigators¹⁵⁻²³ relatively little attention has been given to the mechanism of the explosive decomposition. Burden and Burgoyne⁷ showed that the decomposition products at room temperature and atmospheric pressure given in Table HI could be most simply explained by assuming the occurrence of two simultaneous reactions having the following overall effects :



It was concluded that during the explosive decomposition of ethylene oxide at room temperature and atmospheric pressure, 69% of the ethylene oxide decomposed in accordance with reaction (1) and 31% in accordance with reaction (2).

Most workers who have investigated the slow non-explosive decomposition of ethylene oxide have agreed that reaction (1) is prominently involved under their experimental conditions and Seddon and Travers¹⁵ found evidence of reaction (2) as a significant parallel reaction. Heckert and Mack¹⁶ and Thompson and Meissner¹⁷ suggested that the following reaction occurs to a small extent, but they did not mention reaction (2).



The results obtained by Burden and Burgoyne could equally well be interpreted by replacing reaction (1) by a similar one involving a larger paraffin molecule such as reaction (3), but they found no evidence of such a reaction and it is certainly less probable than reaction (1).

The decomposition products obtained when ethylene oxide vapour, initially at a temperature of 70°C, is burnt in absence of air at atmospheric pressure in a flat flame burner²⁵ are given in Table III together with those formed when ethylene oxide is decomposed in a rocket motor²⁴ at a chamber pressure of 750±50 lb/in² abs. For comparison the analyses obtained during the course of the present investigation have been converted to an ethylene oxide free basis.

It may be seen from Table III that the chief effects of pressure are to increase the amount of methane and to

decrease the amount of ethylene formed as a result of the decomposition. The heat liberated by reaction (1) is 32.11 Kcal/mole whereas that by reaction (2) is only 7.98 K cal/mole. Thus the effect of pressure is to increase the overall heat of reaction. In addition to the gaseous products listed in Table III, solid carbon combined with a variable amount of hydrogen was deposited in the vessel at pressures in excess of atmospheric. It appears likely that this was formed by the exothermic pyrolysis of ethylene.

TABLE III.—Effect of Pressure on the Gaseous Decomposition Products of Ethylene Oxide

Constituent	Flat Flame ²⁵ (%)	Flame propagation ⁷ (%)	Explosive decomposition (%)		Rocket motor ²⁴ (%)
H ₂	19.6	12.7	16.4	16.1	9.5
CO	44.3	46.6	48.7	47.1	48.5
O ₂	—	—	—	0.2	—
CH ₄	25.9	32.2	32.2	35.2	39.9
C ₂ H ₆	—	—	1.3	1.0	2.1
CO ₂	—	1.0	0.2	0.3	—
C ₂ H ₄	10.2	7.5	1.2	—	—
P ₁ (lb/in ² abs)	14.7	14.7	45	135	750±50

The laminar burning velocity of ethylene oxide vapour in absence of air at atmospheric pressure as measured in a flat flame burner²⁵ was only 4 cm/s ; this accounts for the slow rate of pressure increase shown in Fig. 6. Although dP/dt is increased as the initial pressure of ethylene oxide vapour is raised, the value at 45-55 lb/in² abs is still only 1300 lb/in² s. In view of this it is surprising that Hess and Tilton¹² were unable to use a bursting disc to relieve the pressure in their vessel.

The most important practical result of this investigation is that a much larger proportion of nitrogen has been found necessary to suppress the explosive decomposition of ethylene oxide than had been suggested by Hess and Tilton¹². Presumably the reason for the widely differing results arises from a difference in the energy transferred to the gas by the two igniting sources. Furthermore the amount of nitrogen as shown in Fig. 7 increases with increasing partial pressure of ethylene oxide vapour in the mixture. This result is to be expected if the proposed mechanism of decomposition is accepted since the heat of decomposition of ethylene oxide will increase with pressure. In addition, pressure has the effect of increasing the burning velocity. Hence the heat losses will be reduced and more nitrogen will be required to absorb the heat liberated by explosive decomposition. Ethylene was not very effective in suppressing the decomposition because some of it decomposed to carbon and hydrogen and in so doing liberated heat. Propane and butane are more effective than nitrogen because of their greater heat capacities.

Since the burning velocity of the ethylene oxide decomposition flame is low, it is to be expected that the ratio of the volume to the internal surface area of the vessel will affect the explosion pressures developed owing to variation in heat losses. This is confirmed by the results given in Fig. 9 from which it may be seen that the ratio P_E/P_1 decreases as the ratio V/A decreases. Having regard to the mechanism of the reaction, thermochemical calculations indicate that the ratio P_E/P_1 will not exceed 10 at high initial pressures, even in vessels having a large volume to surface-area ratio,

Conclusions

It has been confirmed that ethylene oxide in the absence of air will undergo explosive decomposition at 125°C and

pressures up to 155 lb/in² abs when ignited with a source of suitable energy. The pressure rise within the vessel depends on the initial pressure of the ethylene oxide vapour and to a certain extent on the size and shape of the vessel. Under similar pressure and temperature conditions propylene oxide vapour was found to be stable but at higher pressures and temperatures it is thought that it too may be made to decompose explosively if ignited.

The use of an inert gas to maintain a non-explosive vapour-phase mixture is the only reliable method of preventing an explosion from ignition sources within a vessel. Although propane and butane are most effective in suppressing the explosive decomposition of ethylene oxide, in practice their use is restricted because of their solubility in liquid ethylene oxide. The proportion of nitrogen needed to suppress the explosibility of ethylene oxide at a partial pressure of 120 lb/in² abs and 125°C is 65%. It must be remembered that a small amount of oxygen or an increase in the partial pressure of ethylene oxide vapour will raise this figure; hence in practice it might be necessary to increase the proportion of nitrogen to, say, 75% to cover these contingencies. This procedure necessitates designing the vessel to withstand a working pressure about four times the partial pressure of the ethylene oxide vapour.

An alternative procedure is to design the vessel to withstand the pressure generated by the products of combustion. Before this can be done with confidence it will be necessary to examine in more detail the effect of the size and shape of the vessel on the maximum decomposition pressure developed. Although it is considered unlikely that the pressure ratio P_2/P_1 in a vessel having a large volume to surface area ratio will exceed 10, the possibility of a detonation cannot be discounted; nevertheless, under conditions of size and pressure similar to those employed in this investigation, this seems unlikely.

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Appendix

Ethylene oxide was supplied by Petrochemicals Ltd. The analysis of the gas was as follows:—

Aldehyde content as acetaldehyde	.. % wt.	0.005
Water content	.. % wt.	<0.01
Hydrolysable chlorine as ethylene dichloride	.. % wt.	0.0037
Acetylene content	.. % wt.	<0.005
Ethylene oxide content	.. % wt.	>99.9

Nitrogen and ethylene were supplied by British Oxygen Gases Ltd. The nitrogen content on a dry basis was 99.9% vol, the oxygen content 0.05% vol, the remainder consisting of the rare gases together with traces of carbon dioxide and hydrogen. The ethylene content on a dry basis was greater than 98% vol, the chief impurities being nitrogen and carbon dioxide.

Butane and propane were supplied by Shell-Mex and B.P. Gases Ltd.

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