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No. 776

STUDIES OF PHOSGENE PRODUCTION DURING
THE THERMAL DECOMPOSITION OF PVC IN AIR

by

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October, 1969.

FIRE RESEARCH STATION

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SUMMARY

The production of phosgene during the thermal decomposition of both a commercial PVC and a relatively pure PVC polymer at temperatures between 250 and 500°C in air has been studied by gas chromatography. Difficulties encountered with the general handling and analysis of phosgene are recorded. Phosgene has not been detected in any experiment and minimum detection limits have been determined by adding known amounts of phosgene to the system during the decompositions. By comparing the detection levels of phosgene with the yields of hydrogen chloride, phosgene is shown to make little contribution to the toxicity of the decomposition products. Some general recommendations are given for sampling fire gases for phosgene studies during large scale tests.

KEY WORDS: Phosgene, plastics, gas chromatography.

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APPENDIX

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1. INTRODUCTION

The production of phosgene from fires involving PVC has been the subject of concern for many years. Small amounts of phosgene have been tentatively reported in the decomposition products of PVC¹ but in general the data of these reports are rather inconsistent.

A detailed study has recently been made of minor products from the thermal decomposition of PVC in air and nitrogen² at temperatures between 300 and 500°C. PVC samples were decomposed in a furnace in a flow system and the condensable products collected in a special stainless steel trap coupled 'on-line' to a gas chromatograph with a conventional gas sampling valve. In this way approximately 75 different products (excluding CO, CO₂, H₂O and HCl) were detected using a flame ionisation detector and shown by retention time experiments and mass spectrometry to consist mainly of aromatic and aliphatic hydrocarbons.

The products were monitored in these earlier experiments over both the primary (dehydrochlorination) and secondary decomposition stages to an overall decomposition time of 30 minutes. These time resolved experiments showed that the products were generated mainly during dehydrochlorination. During decompositions in air, the presence of oxygen altered the quantitative yields of products but there was no evidence of oxygenated organic materials.

In general, the flame ionisation detector used in the above studies is insensitive to inorganic materials. Because of this and the high toxicity of phosgene, experiments to specifically monitor the production of phosgene during the decomposition of PVC were undertaken using a thermal conductivity detector.

Preliminary experiments to study the behaviour of phosgene in the decomposition system and various chromatographic aspects of phosgene are outlined. In these experiments a variety of problems were encountered, associated with the loss of phosgene in the decomposition system and the chromatograph and these problems are recorded in detail.

The experimental results for a study of phosgene production from the thermal decomposition of both a commercial PVC and a PVC polymer in air at temperatures between 250 and 500°C are given.

A brief toxic appraisal of the contribution of phosgene to the overall toxicity of the decomposition products is presented. Finally, some general recommendations for the analysis of phosgene in fire gases are given.

2. EXPERIMENTAL

(i) The Decomposition System

The decomposition system has been recently outlined in detail². For convenience, the essential features of the apparatus relevant to the phosgene studies are shown in Figure 1 and briefly described below.

Samples of PVC (15 mg) are decomposed in a small ceramic boat which is injected into the furnace by the influence of an external magnet on the steel plug P. During the decomposition a flow of air (100 ml/min at 20°C) is maintained through the silica furnace tube and carries the volatile decomposition products along the heated outlet tube and into a stainless steel gas sampling valve coupled in the usual way to the inlet of a gas chromatograph. For the collection of the decomposition products, the air from the furnace tube is directed through the collecting loop (stainless steel tubing; 3.2 mm O.D.) and the phosgene, together with other condensable products, is trapped out of the air stream by surrounding the loop with isopentane cooled with liquid nitrogen. The collection temperature is monitored by a thermocouple silver-soldered to the base of the loop and controlled manually by raising or lowering the liquid nitrogen vessel. During the collection period an internal bypass in the valve maintains the supply of helium carrier gas to the chromatograph.

After collection, the valve is turned to the 'inject' position, the refrigerant is removed and replaced quickly by a fluidised sand bath thermostatted at 150°C. In this way the trapped products are vaporised quickly and carried by the helium into the chromatograph for analysis.

The stainless steel valve and the flow lines coupling the valve to the furnace tube and chromatograph respectively are controlled at about 100°C in order to avoid problems from the absorption and condensation of products prior to chromatography.

(ii) Chromatography

A Hewlett-Packard 5750 Research Chromatograph fitted with simultaneous dual flame ionisation and thermal conductivity detectors was used. Phosgene was monitored using the thermal conductivity detector but the flame detector assisted in monitoring products eluted near to phosgene. Analyses were performed using a silicone grease column; the operating conditions of this column are given below:-

Silicone grease on Chromosorb P. (Perkin Elmer Column material No. 496.0769). 3 m x 3.2 mm in stainless steel, temperature programmed at 2°C/min from 30°C (Helium carrier gas, 30 ml/min).

Some preliminary experiments were performed using a Porapak Q column (2 m x 3.2 mm), temperature programmed at 4°C/min from 30°C to 250°C (Helium carrier gas, 30 ml/min).

(iii) Materials

The commercial PVC was cut as small cubes (3 to 4 mg each) from a rigid sheet of the type used to study the behaviour of PVC in fires³. According to the manufacturers of the PVC the sheet contained approximately 10 per cent of organic and inorganic additives by weight.

A relatively pure PVC emulsion polymer in powder form was also used. A total sample weight of 15 mg was used in all decomposition experiments.

The phosgene for calibration purposes was obtained as a commercial 12% solution in benzene. For use, the material was diluted to a 6% solution of phosgene in a benzene toluene mixture.

3. RESULTS

(i) Preliminary Experiments on the Chromatography of Phosgene

Before undertaking direct studies to monitor the production of phosgene during the thermal decomposition of PVC in air, a series of preliminary experiments were undertaken to investigate the retention time and general peak shape of phosgene eluted from the chromatograph. For this study small samples of the phosgene solution (1 µl) were injected directly into the inlet port of the chromatograph in the conventional manner. Studies were made using the silicone grease and Porapak columns in turn. These columns had been used successfully to separate and examine the many minor decomposition products (generally hydrocarbons) from PVC as outlined earlier².

For the phosgene experiments, the columns were both temperature programmed using the operating conditions as found experimentally in this earlier work to be the optimum conditions for separating the hydrocarbons. These operating conditions were used since the detection of phosgene during actual PVC decomposition experiments would depend to a great extent on the resolution of materials eluted near to phosgene during chromatography.

Using the silicone grease column the phosgene peak was detected with good peak shape by the thermal conductivity detector as shown in Figure 2. Toluene, eluted after benzene is omitted for convenience. Only benzene and toluene could be detected with the flame ionisation detector although a disturbance of the base line at the phosgene retention time was noted under high sensitivity.

On the Porapak Q column, phosgene was not detected by thermal conductivity even after the column had been operated at the upper temperature limit of 250°C for a considerable time.

At elevated temperatures phosgene is reported to be a strong chlorinating agent and attacks various metals and metallic oxides including iron⁴. An interaction of this kind could explain the absence of phosgene during the Porapak experiment. Assuming that materials are retained on this column according to their molecular size, then phosgene should have been eluted near to toluene with a retention time of about 50 minutes with elution at approximately 200°C.

On the silicone grease column, phosgene is eluted at 40°C with a retention time of approximately 4 minutes. It seems probably that phosgene is decomposed in the stainless steel column during elution from Porapak Q.

(ii) General Loss of Phosgene in the Decomposition System

Because of the loss of phosgene during chromatography with the Porapak column, a series of experiments were undertaken to examine possible losses of phosgene in the furnace and stainless steel components of the decomposition system.

For these experiments 0.5 - ml samples of the vapours directly above the benzene-toluene mixture in the storage vessel were extracted with a syringe and injected through the rubber cap into the decomposition equipment. These samples would be relatively rich in phosgene compared with benzene and toluene.

In this work the gas sampling valve and associated flow lines were maintained at 100°C. Isopentane cooled to -160°C was used as a refrigerant for the collecting loop and the residual phosgene after passing through the decomposition equipment was monitored using the silicone grease column.

With the furnace at 100°C the phosgene peak could be clearly detected by thermal conductivity but the peak height was only about one third of the expected value based on direct injection into the chromatograph. Clearly a considerable loss occurs during the contact time in the hot decomposition system. As the furnace temperature was increased the phosgene peak height decreased rapidly as shown in Figure 3. Phosgene is recorded as a phosgene-benzene peak height ratio. Although consistent amounts of phosgene could be injected into the furnace using the syringe technique the use of this ratio eliminated any errors in the sampling of vapour-air mixtures above the phosgene solution.

(ii) Mechanism of Phosgene Loss in Furnace Section

(a) Possible reaction with benzene and toluene

In the above experiments, phosgene was introduced into the furnace as a mixed vapour with benzene and toluene. Assuming equal area sensitivities of these three materials on the thermal conductivity detector, direct gas chromatographic analysis of samples showed the amount of phosgene to be initially between two and three times greater than the combined amount of benzene and toluene. A temperature dependent interaction between phosgene and benzene, or toluene, was considered as a possible explanation for the losses of phosgene in the furnace section but discounted for two main reasons. Firstly, at 400°C, although there is a quantitative loss of phosgene, the benzene and toluene peak heights are not appreciably altered. Secondly no reaction products were detected either by the thermal conductivity or the flame ionisation detectors.

The absence of gas phase reactions of this kind also suggests that any phosgene formed during the decomposition of PVC would not be lost by secondary gas phase interactions with the many hydrocarbon products.

(b) Pyrolysis of Phosgene in the Furnace

Phosgene can be synthesised by the interaction of carbon monoxide with chlorine; a reaction known to be reversible at high temperatures. At temperatures between 500 and 800°C the equilibrium amount of phosgene decomposed is⁵:-

TEMPERATURE	(°C)	503	553	603	800
AMOUNT DECOMPOSED	(%)	67	80	91	100

Also, at 503°C, there is approximately 15 per cent dissociation of phosgene within 1 minute. At an air flow rate of 100 ml/min the contact time of phosgene in the furnace is about 0.5 minutes at 400°C and clearly the temperature dependence of Figure 3 is inconsistent with a pyrolytic loss of phosgene. Also chlorine should have been detected in a pyrolytic loss but no such peak was apparent.

c) Surface Effects

Although phosgene does not react directly with silica⁴, the decomposition tube was removed and replaced with a Pyrex tube. This tube immediately produced improved yields of phosgene as shown by the dotted line in Figure 3. The reason for this increase is not fully understood but on removal the silica tube was slightly contaminated with a white powder thought to be titanium dioxide, a known additive to the commercial PVC. Titanium dioxide is readily chlorinated with phosgene at elevated temperatures⁵ and a loss of this nature would explain the absence of reaction or decomposition products readily detected by chromatography.

However, even with the Pyrex tube, the losses of phosgene at different temperatures in the furnace section are still too great to be accounted for by a pyrolytic mechanism. An interaction of phosgene with either the borosilicate glass or impurities in the glass may be responsible for this loss.

Using the Pyrex tube, phosgene could be monitored at furnace temperatures up to 500°C and experiments were undertaken to study the production of phosgene during the decomposition of PVC in air.

(iv) Phosgene Production from a Commercial PVC

Phosgene production from a commercial PVC sample was measured at 50°C intervals from 250 to 500°C. In all experiments phosgene was monitored for a total of 30 minutes although in certain cases this was sub-divided into two periods.

At 400 and 450°C, experiments were performed over the primary (dehydrochlorination) and secondary decomposition stages. At each temperature the primary products were collected at -130°C and the secondary products at -160°C. The collecting temperature of -130°C during the primary stage ensured that phosgene would be collected without trapping an appreciable quantity of hydrogen chloride, since large amounts of this latter material interfered with the analysis of phosgene. During the secondary decomposition stages, the trap temperature was reduced to -160°C (F.Pt of isopentane) to assist the collection efficiency.

In studies at 300 and 350°C one experiment only was performed for each temperature where the collection trap was maintained at -130°C for the primary or dehydrochlorination stage and then reduced to -160°C for the following secondary decomposition stage. In the experiment at 250°C, hydrogen chloride was evolved over the whole 30 minute period and the collection trap maintained at -130°C throughout.

At 500°C, the PVC was completely oxidised to a non combustible ash within 10 minutes, and the collection trap maintained at -130°C throughout this period.

Phosgene was not detected in any of these experiments. Each experiment was repeated under identical conditions but with a known amount of phosgene initially added to the furnace section. This seeding technique ensured that the detection level of phosgene was known for each experiment. The detection level was calculated by comparing the chromatographic traces of the decomposition products and visually estimating the minimum peak height of phosgene which would be readily detected above the baseline pattern in the actual (i.e. non-seeded) experiment.

In each case the phosgene was introduced into the furnace section with a syringe as outlined previously. The gaseous sample contained $0.1 \pm .01$ mg of phosgene as estimated by injecting samples directly into the chromatograph and comparing the peak height with that of a known volume of 6% phosgene solution.

A summary of the experimental results for the phosgene experiments between 250 and 500°C and the estimated detection levels are shown in Table 1. Figure 4 shows the chromatographic traces of the primary decomposition stage (0 to 4.5 mins) at 400°C with and without added phosgene using the thermal conductivity detector. Also shown, for comparison, are the equivalent flame ionisation traces recorded simultaneously with the thermal conductivity data. The thermal conductivity traces show the detection of phosgene without interference from hydrogen chloride by collection at -130°C.

TABLE 1

Phosgene studies during the decomposition
of a commercial PVC at 250 to 500°C

Temp (°C)	Decomposition Stage P = Primary S = Secondary	Experimental Time (mins)	Collection Temp (°C)	Phosgene Detection ND= = Not Detected	Detection Limit (mg)
250	P	0 - 30 *	-130	ND	0.01
300	P + S	0 - 30 ^φ	-130 and -160	ND	0.005
350	P + S	0 - 30 ^φ	-130 and -160	ND	0.002
400	P	0 - 4.5	-130	ND	0.0015
	S	4.5 - 30	-160	ND	0.0015
450	P	0 - 4.0	-130	ND	0.003
	S	4.0 - 30	-160	ND	0.01
500	P + S	0 - 10 [≡]	-130	ND	0.01

* Incomplete primary stage

^φ Primary stage 0 to 9 mins at 300°C; 0 to 5.0 mins at 350°C

[≡] Complete burn-out after 10 minutes

(v) Phosgene production from a PVC Polymer

The commercial PVC studied in section 3 (iv) contains approximately 10 per cent by weight of various additives. One of these additives, titanium dioxide, was thought to be partly responsible for the phosgene loss in the silica decomposition tube. Small amounts of phosgene generated by the thermal decomposition of the commercial PVC might be removed by reaction with these additives and the absence of phosgene during these tests could be misleading.

In order to investigate the effect of these additives the experiments of section 3 (iv) were repeated using a relatively pure PVC emulsion polymer. Again, seeding experiments ensured that the detection level of phosgene was known for each experiment. The data for these experiments are shown in table 2. Phosgene was not detected in any experiment. In general, since larger amounts of products are produced from the pure polymer, the detection levels given in table 2 are larger than those of the commercial material.

TABLE 2

Phosgene studies during the decomposition
of a PVC Polymer at 250 to 500°C

Temp (°C)	Experimental Time (Mins)	Collection Temp (°C)	Phosgene Detection ND = Not Detected	Detection Limit (mg)
250	0 - 30 *	-130	ND	0.005
300	0 - 30 †	-130 and -160	ND	0.002
350	0 - 30 †	-130 and -160	ND	0.002
400	0 - 4.5	-130	ND	0.003
	4.5 - 30	-160	ND	0.005
450	0 - 4.0	-130	ND	0.01
	4.0 - 30	-160	ND	0.01
500	0 - 10 ‡	-130	ND	0.03

* Incomplete primary stage

† Primary stage 0 to 9 mins at 300°C; 0 to 5.0 mins at 350°C

‡ Complete burn out after 10 minutes

4. DISCUSSION

Phosgene is a difficult material to handle and analyse quantitatively. In general at temperatures in excess of 200°C it appears to be rapidly destroyed by stainless steel as shown by chromatography. It reacts with Pyrex showing a rapid and complete loss at temperatures above 500°C. In the silica decomposition tube the quantitative loss at 400°C was attributed partly to a reaction with titanium dioxide, an additive to the commercial PVC.

In actual fires, where samples of the fire gases are extracted through long tubes for the remote analysis of phosgene, great care needs to be taken to avoid misleading data. The results in this report suggest that approximately 100°C is an optimum temperature for the collection tube to avoid absorption problems and excessive loss of phosgene by reaction. Glass appears to be better than stainless steel for the tube material and the contact time of gases inside the tube should be as short as possible.

However, even under these conditions a tube could produce serious losses of phosgene during sampling. A reliable solution of the problem is to calibrate the system by injecting known concentrations of phosgene throughout the whole sampling system and experimentally determining the sampling efficiency.

In this report, phosgene has not been detected during either the primary or secondary decomposition stages in studies of both a commercial PVC and a PVC polymer at decomposition temperatures between 250 and 500°C. Direct seeding experiments ensured that the detection level at each temperature was known.

A brief comparison of the toxicity of phosgene at the least sensitive detection level to the toxicity of hydrogen chloride for the commercial PVC was presented in an earlier report². For this evaluation, hydrogen chloride was chosen as a reference material rather than carbon monoxide for convenience since at temperatures in excess of 300°C dehydrochlorination is considered to be a rapid and quantitative process.

For these comparisons a toxicity factor T was used⁶ and defined as

$$T = C_E / C_F$$

where C_E = Experimental concentration in p.p.m. produced from
1 gram of PVC in a metre cube

C_F = concentration in p.p.m. fatal in a short exposure

The toxicity factor for phosgene and hydrogen chloride from the commercial material are given in table 3.

TABLE 3

Toxic parameters for hydrogen chloride
and phosgene from the commercial PVC

	Yield per 15 mg (mg)	Yield per gram (mg)	C _E (p.p.m)	C _F (p.p.m)	Toxicity Factor (T)
Hydrogen Chloride	7.6	505	338	1500	2.25×10^{-1}
Phosgene 1 *	0.01	0.66	0.163	50	3.26×10^{-3}
Phosgene 2 *	0.0015	0.10	0.0247	50	4.94×10^{-4}

* Estimated detection levels

The value for hydrogen chloride is based upon complete dehydrochlorination².
Two values of T are quoted for phosgene for the extreme values of the
detection levels (0.01 mg and 0.0015 mg). C_F values are taken from the
literature⁷.

The equivalent toxicity factors for the PVC polymer are given in table 4.

TABLE 4

Toxic parameters for hydrogen chloride
and phosgene from the PVC polymer

	Yield per 15 mg (mg)	Yield per gram (mg)	C _E (p.p.m)	C _F (p.p.m)	Toxicity Factor (T)
Hydrogen Chloride	8.75	582	392	1500	2.61×10^{-1}
Phosgene 1 *	0.03	2.0	0.495	50	9.9×10^{-3}
Phosgene 2 *	0.002	0.133	0.033	50	6.6×10^{-4}

* Estimated detection levels

The theoretical yield of hydrogen chloride is somewhat greater than in the
commercial case due to the absence of additives in the pure polymer.

In both the commercial PVC and the PVC polymer the contribution, even assuming the worst detection level in each case, of phosgene to the overall toxicity of phosgene and hydrogen chloride is small. Possible synergistic effects of phosgene with hydrogen chloride are unknown but taking into account the relative amount of each material, effects of this kind would have to be large in order to be important. The value for C_F for hydrogen chloride (1500 p.p.m) used in this report is based on a value which is immediately hazardous to life. However due to the acrid nature of the gas, atmospheres containing as low as 100 p.p.m. can be very difficult to inhale⁸. The level likely to be dangerous in a fire may therefore be much lower than 1500 p.p.m. The adoption in this report of a C_F value of 1500 p.p.m. for hydrogen chloride introduces a further safety margin to the contribution of phosgene to the overall toxicity of the decomposition products.

Finally, the substantial loss of phosgene using the silica decomposition tube, attributed to an interaction between phosgene and titanium dioxide, could be used to advantage in practice. Trace amounts of phosgene below the detection level of this work could be removed by a suitable choice of additives to the commercial plastic.

5. CONCLUSIONS

1. Phosgene is a difficult material to handle and analyse due to interactions, particularly at elevated temperatures, with glass, metals and metallic oxides.
2. Phosgene has not been detected in this work by gas chromatography during the decomposition of both a commercial PVC and a PVC polymer in air at temperatures between 250 and 500°C. The detection levels of phosgene were estimated using a seeding technique.
3. Even if present at the detection levels the toxic hazard of phosgene, neglecting synergistic effects, in the decomposition products is very small compared to that from hydrogen chloride.

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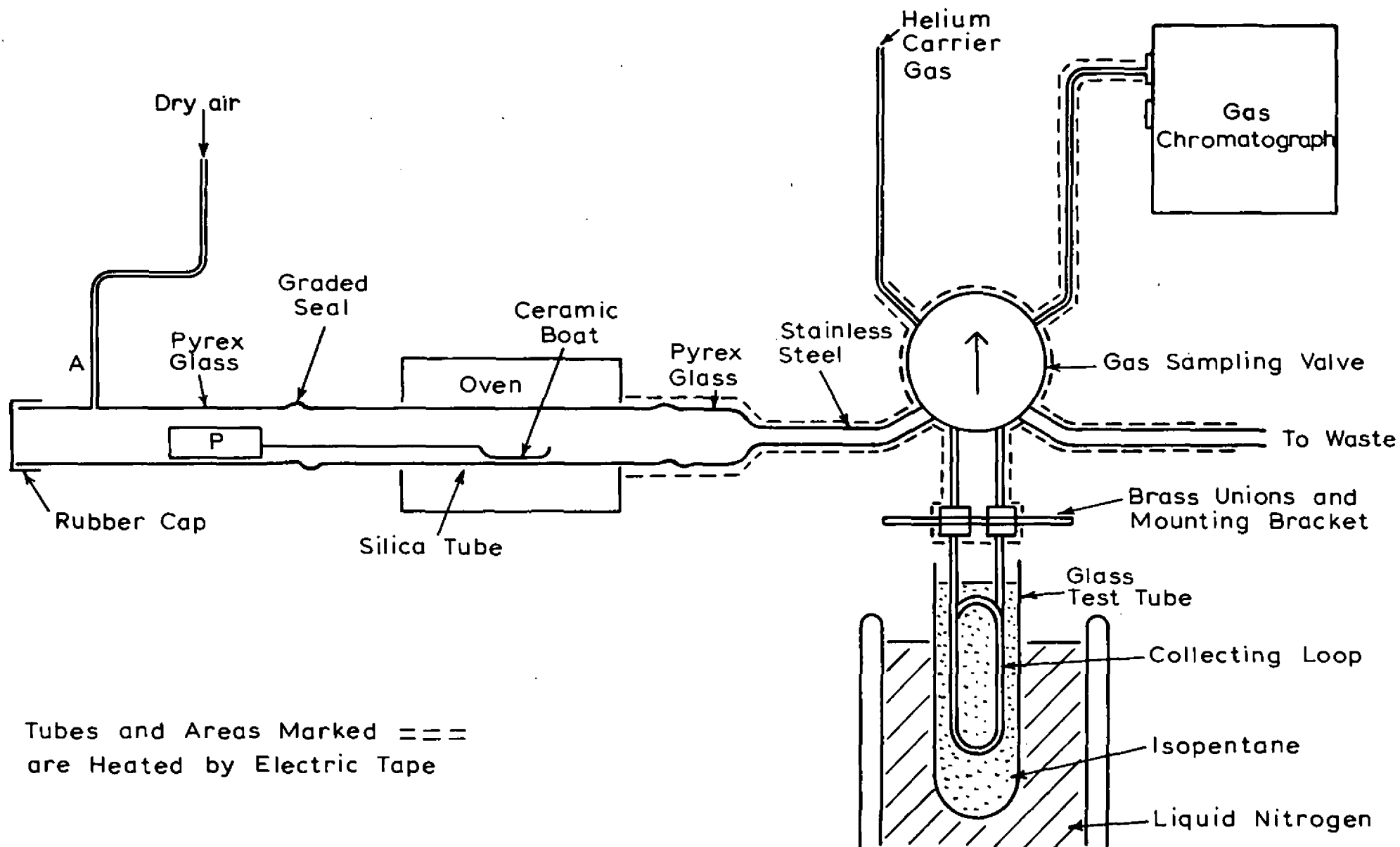


FIG. 1. THE DECOMPOSITION SYSTEM

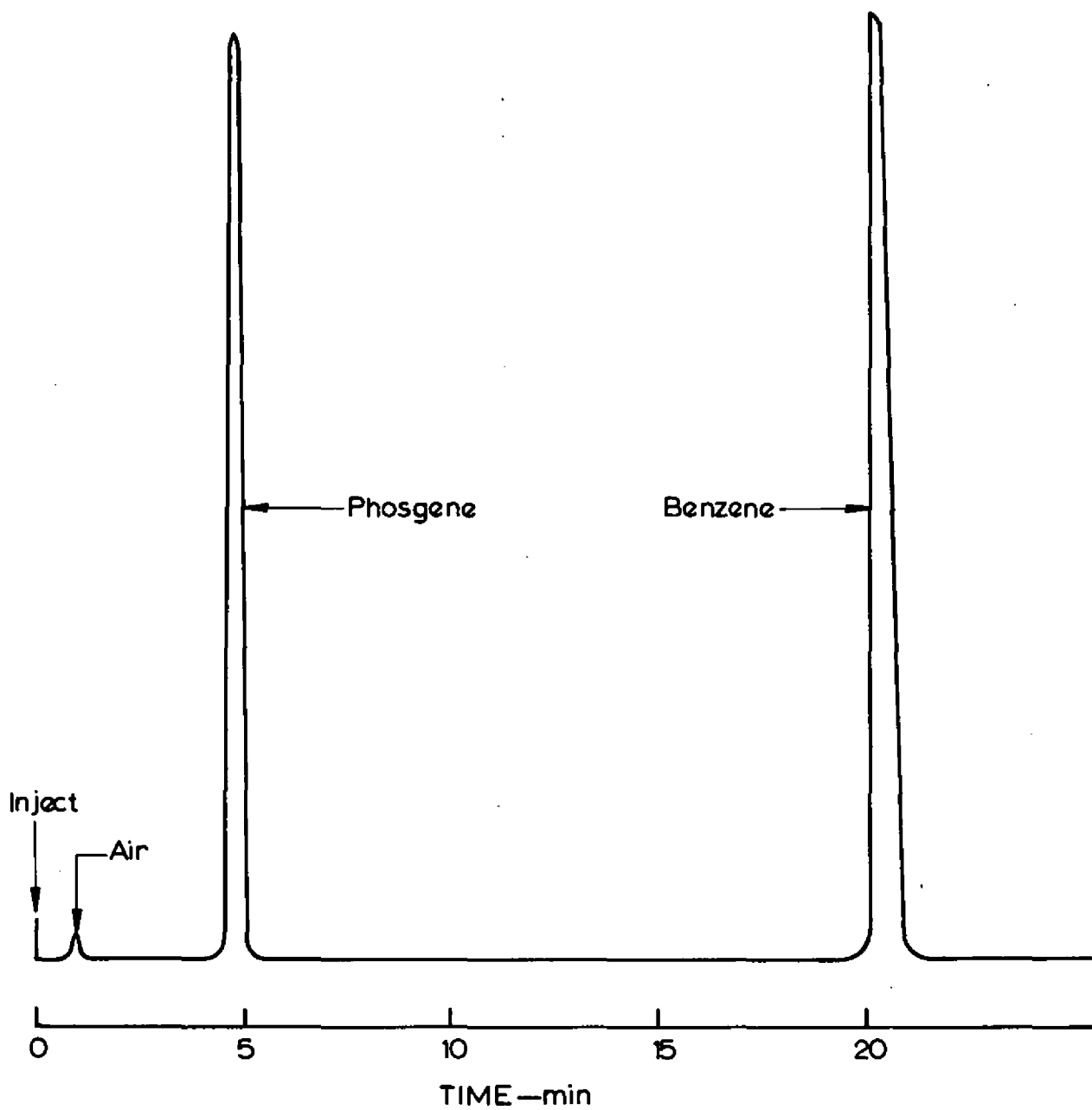


FIG. 2. CHROMATOGRAPHIC TRACE OF PHOSGENE USING THE THERMAL CONDUCTIVITY DETECTOR

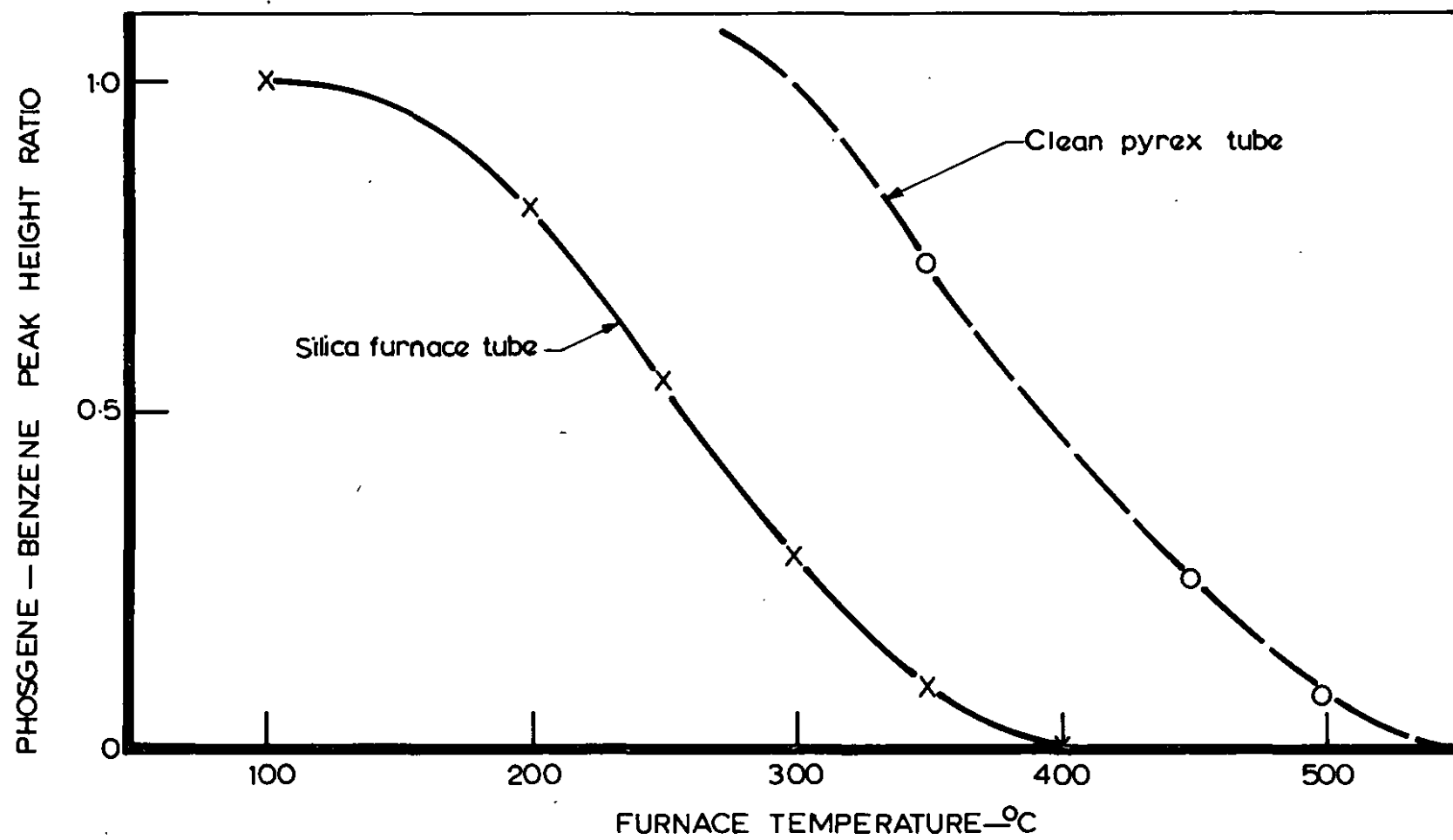
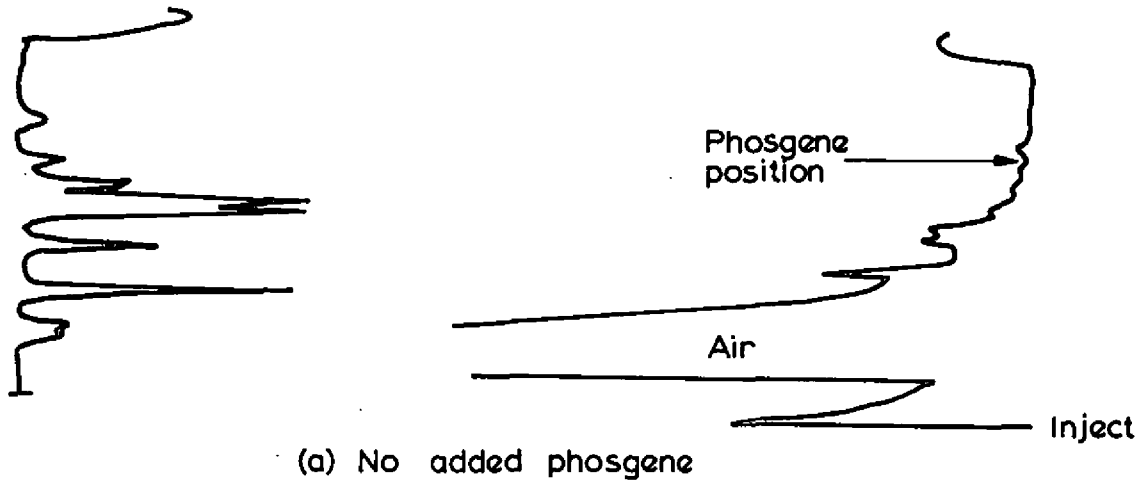


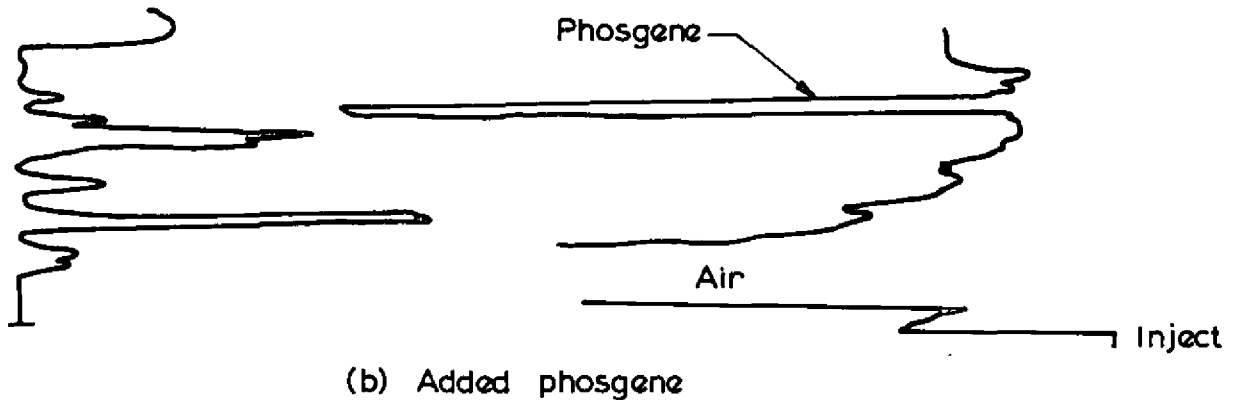
FIG. 3. TEMPERATURE DEPENDENCE OF PHOSGENE IN THE FURNACE SECTION

Flame ionisation

Thermal conductivity



(a) No added phosgene



(b) Added phosgene

FIG. 4. CHROMATOGRAPH TRACES OF THE PRIMARY DECOMPOSITION PRODUCTS OF COMMERCIAL P.V.C. AT 400 °C

