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The thermal degradation of aromatic polyimides in nitrogen at 700°C

- by -

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SYNOPSIS

The thermal degradation of aromatic polyimides in nitrogen at 700°C was studied using pyrolysis gas chromatography, infra red spectroscopy, and radiochemical techniques. Degradation mechanisms were postulated to account for the breakdown products found. Particular attention was paid to the ratio of CO_2/CO evolved during pyrolysis and this was found to vary with the moisture content of the polyimide and with the pyrolysis temperature.

Acknowledgements

The authors acknowledge the fellowship from the Ministry of Technology under which this work was carried out, and wish to thank Dr.W.W. Wright and Mr. R.A. Dine-Hart of R.A.E. Farnborough for supplying some of the polyimide samples.

The Thermal Degradation of Aromatic Polyimides in Nitrogen

Introduction

Aromatic polyimides (Fig. 1) have been well publicised as 'high temperature polymers', [1-5] and although their behaviour at high temperatures has been studied [1-11], the mechanism of their thermal degradation is not well established.

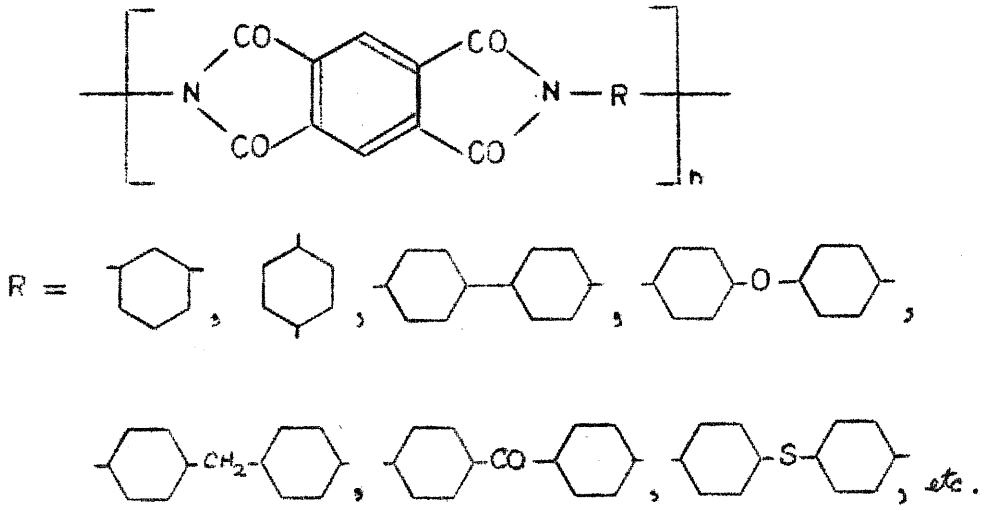


FIG. 1 AROMATIC POLYIMIDES.

A number of workers have carried out thermogravimetric analyses on polyimides in air and in various inert atmospheres. [1-3, 6-11]. Bruck,[7] and Heacock and Berr[2] have collected and identified volatile degradation products, and Bruck has also investigated the nature of the 'tar' and the 'char' which are formed on pyrolysis in inert atmospheres.[7,8]

As a result of these studies, which are summarised in Tables I and II, it is known that aromatic polyimides begin to break down between 450 and 500°C in air and between 500 and 600°C in inert atmospheres, depending on the nature of R (Fig. 1) and on the purity of the cured polymer.

TABLE I

Summary of publications relating to

the thermal degradation of polypyromellitimides

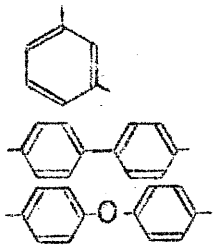
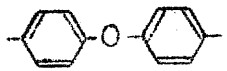
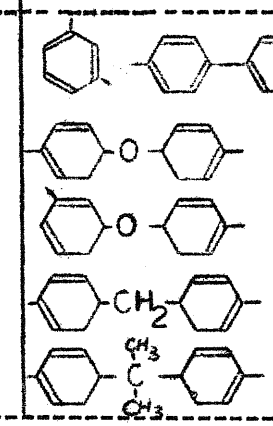
Authors	Nature of R (Fig. 1)	Source of Polyimides	Type of Degradation Study	Atmospheres	Comments on Results
Idris Jones,[1] Ochynski and Rackley		Authors (National Chemical Laboratory, Teddington).	T.G.A.	Air and Argon	$-\frac{dw}{dt}$ vs T plots
Heacock and Berr[2]		E.I. du Pont de Nemours and Co. Inc. (H-film)	T.G.A. Pyrolysis/ (2hr 540°C) Mass Spec.	Air and Helium Vacuum (closed system)	ΔE_{air} = 39.9 k cal ΔE_{He} = 54.0 k cal. Analysis of products Table II
Freeman, Frost, Bower and Traynor[3]		Westinghouse Research Laboratories	T.G.A.	Air	Stabilities of various R's compared

TABLE I (Continued)

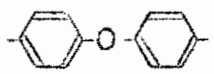
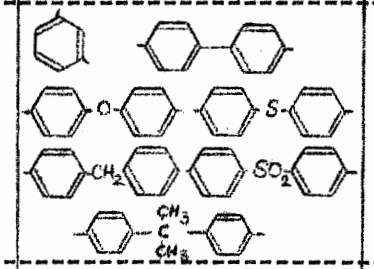
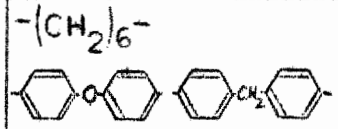
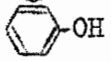
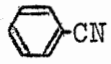
Authors	Nature of R (Fig. 1)	Source of Polyimides	Type of Degradation Study	Atmospheres	Comments on Results
Bruck[6,7,8]		E.I. du Pont de Nemours and Co. Inc. (H-film)	T.G.A. Pyrolysis (600°C 4 hr)	Air and Vacuum Vacuum (a)Trap products (i)Purified H-film (ii)Standard H-film (b) Closed System (Standard H-film)	ΔE_{air}=33k cal. ΔE_{vac}=74k cal. Analysis of products Table II
Sroog[9]		E.I. du Pont de Nemours and Co. Inc.(Film and Plastics Dept.)	T.G.A.	Air Helium	Stabilities of various R's compared
Nishizaki and Fukami[10,11]		Mitsubishi Electric Corp.	T.G.A. and I/R	Air and N_2	R aliphatic and aromatic compared
Cotter and Dine-Hart[12]	Model compounds aromatic imides	R.A.E. Farnborough	Electron impact/ mass spec.	Vacuum	Indication that CO_2 is a major degradation product.

TABLE II

Mass Spectrometric Analysis of

Volatile Degradation Products of Aromatic Polyimides

Author	S.D. Bruck[7]			Heacock and Berr[2]
Experimental Details	Standard H-film 610°C. 4 hours 10^{-5} mm Hg. closed system	Standard H-film 600°C 4 hrs 10^{-3} mm Hg. Liquid N_2 traps (- 196°C)	Purified H-film 600°C. 4 hrs 10^{-3} mm. Hg. Liquid N_2 traps (-196°C)	Standard H-film 540°C 2 hrs. Vacuum Closed system
Volatile Products Mole %				
H_2	9.0	not trapped	not trapped	2.6
CH_4	1.1	not trapped	not trapped	none
NH_3	1.2	2.1	none	trace
H_2O	7.6	53.0	72.6	1.2
HCN	1.3	5.6	none	1.2
CO	60.5	not trapped	not trapped	58.7
CO_2	19.0	38.0	25.4	35.1
	0.3	0.6	0.4	0.7
	0.02	0.04	0.2	none
	0.06	0.06	0.1	0.5

The major volatile degradation products are carbon monoxide and carbon dioxide but the relative quantities of these products vary widely with pyrolysis conditions and sample purity (Table II).

Little effort has been made to establish the mechanisms of the formation

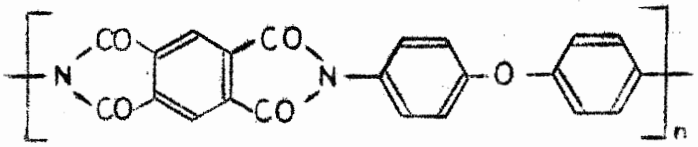
of these products, but some suggestions have been put forward. Bruck[7] suggests that carbon monoxide is evolved as a result of primary cleavage of carbonyl carbon - nitrogen bonds followed by cleavage of aromatic-carbonyl carbon bonds. He also suggests that carbon dioxide is formed by elimination from polyamic acid remaining as impurity in the polyimide.

The quantities of carbon dioxide found seem too large to be accounted for in this way however, and it seems likely that it is also eliminated from imide groupings. In fact Cotter and Dine-Hart[12] found that carbon dioxide is a major breakdown product when aromatic imides are subjected to electron impact. Since it has been established that strong similarities often exist between the thermal breakdown of molecules and breakdown brought about by electron impact in the mass spectrometer,[13-15] the work of Cotter and Dine-Hart may be taken as strong evidence for the evolution of carbon dioxide from imide groupings in polyimides at high temperatures.

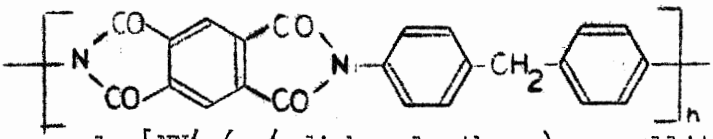
In the present work pyrolysis gas chromatography has been used in conjunction with other analytical techniques to obtain further information on the thermal degradation of polyimides in inert atmospheres.

Materials

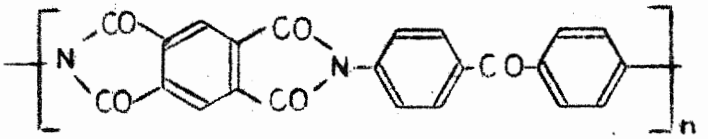
The three different polyimides used in this work were supplied by Wright and Dine-Hart of the Royal Aircraft Establishment, Farnborough in film form. The samples are referred to as DDE/PMDA, DDM/PMDA and DBPh/PMDA where:

DDE/PMDA = 

poly-[NN'-(pp'-diphenylether)pyromellitimide]

DDM/PMDA = 

poly-[NN'-(pp'-diphenylmethane)pyromellitimide]

DBPh/PMDA = 

poly-[NN'-(pp'-benzophenone)pyromellitimide]

Infra red spectra of these materials are shown in Figs. 2-4, the principle absorptions have been discussed elsewhere [9] and will not be enlarged on here. A sample of DDE/PMDA was prepared in these laboratories using pyromellitic dianhydride (PMDA) which was ^{14}C labelled at the carbonyl groups, this sample is referred to as DDE/PMDA*.

Experimental details for the preparation of these materials are reported in the literature [16]; the sample of ^{14}C labelled PMDA was prepared by Yarsley Research Laboratories, Chessington, Surrey.

Experimental

Polyimide samples were pyrolysed on an electrically heated nichrome filament in a stream of nitrogen which was also the carrier gas for the gas chromatograph. A fixed pyrolysis temperature of 700°C was used except when the effect of pyrolysis temperature on the relative quantities of volatile degradation products was being studied. The sample size was varied between 5 and 30 mg with no apparent change in the relative amounts of the pyrolysis products. A variety of columns, oven temperatures and

carrier gas flow rates were used for separating pyrolysis products. Typical pyrograms are shown in Figs. 5-7 together with the column details and operating conditions.

Separated degradation products were identified by their retention times and by infra red spectroscopy where possible. The ^{14}C labelled CO and CO_2 evolved from DDE/PMDA* were detected and estimated using a flow through scintillation counter and integrator connected to the exit port of the gas chromatograph. This assembly, has been described in detail elsewhere.[17]

Results and discussion

Volatile degradation products

The volatile degradation products identified by us for the three polyimides are listed in Table III. Possible mechanisms for their formation are suggested at the end of this section.

Table III

Volatile degradation products of aromatic polyimides

DDE/PMDA	DDM/PMDA	DBPh/PMDA
Hydrogen	Hydrogen	Hydrogen
Carbon monoxide	Carbon monoxide	Carbon monoxide
Methane	Methane	Methane
Carbon dioxide	Carbon dioxide	Carbon dioxide
Unknown (HCN?)	Unknown (HCN?)	Unknown (HCN?)
Water	Water	Water
Benzene	Benzene	Benzene
Phenol	Toluene	Benzonitride
Benzonitride	Benzonitride	

High boiling degradation products

The high boiling degradation products or tars which condensed on the walls of the pyrolysis tube were dissolved in acetone and transferred to an agate mortar. The acetone was evaporated and the tars were ground with dried KBr and pressed into discs for I/R analysis. The I/R spectra of these tars are shown in Figs. 8-10, they suggest that the tars consist largely of short fragments of polyimide chains probably with N-H, $-NH_2$ or $-C\equiv N$ end groups. The characteristic imide absorptions at 1780 cm^{-1} and 720 cm^{-1} are still discernible in all three tar spectra. The principle absorptions of DDE/PMDA at 1725 cm^{-1}, 1500 cm^{-1}, 1375 cm^{-1} and 1230 cm^{-1} are still present in the DDE/PMDA tar, and similarly the principle absorptions of the other tars correspond to absorptions of the original polymers. All three tars have an absorption band at 3350 cm^{-1} which corresponds to the N-H stretching frequency and suggests N-H or possibly $-NH_2$ end groups. This peak is much smaller in the spectra of the original polymers and should not be confused with the O-H bands at 3450 and 3600 cm^{-1} which are discussed later. The tars also have an absorption at 2250 cm^{-1} which may be due to $-C\equiv N$ end groups.

Solid residues or chars

The nature of the solid residue which remained on the pyrolyser wire after pyrolysis was studied by weighing, by elemental analysis, and by I/R spectroscopy.

Approximate weight loss experiments showed that the polyimides all lost about 40% by weight on complete pyrolysis at 700°C in nitrogen. A typical elemental analysis gave C, 78.8%; H, 2.79%; N, 5.87%; O, (by difference) 11.54% for a DDE/PMDA char. The original DDE/PMDA requires

C, 69.1%, H, 2.62%; N, 7.33%; O, 20.94%. The I/R spectrum of a typical char is shown in Fig. 11.

The elemental analyses of the chars were consistent with the loss of large quantities of CO and CO_2, and also indicated a considerable loss of nitrogen. The quantities of benzonitrile detected amongst the volatile products were not sufficient to account for this loss, and since the predominant odour of the volatiles was that of a cyanide it seems likely that some nitrogen was lost as HCN although the latter was not positively identified in this work.

Before discussing possible mechanisms for the formation of the various degradation products it is important to consider the effect of uncyclised units in the polymer chain. Any polyimide sample contains more or less uncyclised material depending on the curing sequence given to the polyamic acid (Fig. 12) precursor.

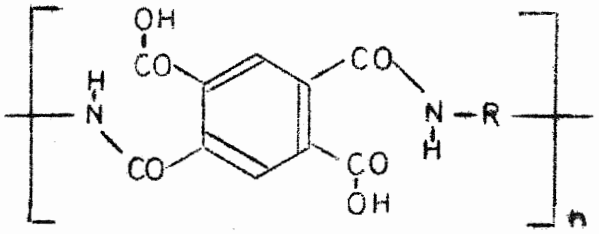


Fig. 12. Polyamic acid structure

Some measure of the number of uncyclised units can be obtained from the I/R spectra of the cured polyimide films. In the detailed spectrum shown in Fig. 13, N-H (stretching) and carboxylic OH (stretching) vibrations give rise to the peaks at 3350 cm^{-1} and 3600 cm^{-1} respectively. Calculations

based on the intensity of the N-H band [18] indicate one uncyclised ring per nine polymer repeat units, assuming that the polymer has no $-NH_2$ end groups. (A fairly safe assumption because a slight excess of anhydride was used in the polymerisation, and also NH_2 groups would almost certainly be destroyed in the final curing stage; 3 minutes at 400°C in air). Similar calculations based on the intensity of the carboxyl OH band indicate one uncyclised ring per eight polymer repeat units.

The absorption band at 3450 cm^{-1} has been assigned to water (O-H stretch) absorbed on the polyimides. On heating to 250°C, 2.0 to 2.5% of water is reversibly desorbed from polyimide films[18], this amounts to about one molecule of water per two polymer repeat units. The assignment of this absorption band to water is strengthened by the fact that it is unaffected by treatment with hot dimethyl sulphate, the peaks at 3600 cm^{-1} and 3350 cm^{-1} being virtually eliminated by methylation[18].

It has already been stated that CO and CO_2 are the major degradation products of aromatic polyimides, and that the ratio CO/CO_2 appears to vary with pyrolysis conditions and polymer purity. In the present work the CO/CO_2 ratio was measured using the radiochemical technique described earlier and it was found that CO/CO_2 varied with pyrolysis temperature and with the moisture content of the polyimide. A typical 'radio-pyrogram' is shown in Fig. 14, and some values of CO/CO_2 are given in Table IV.

Table IV

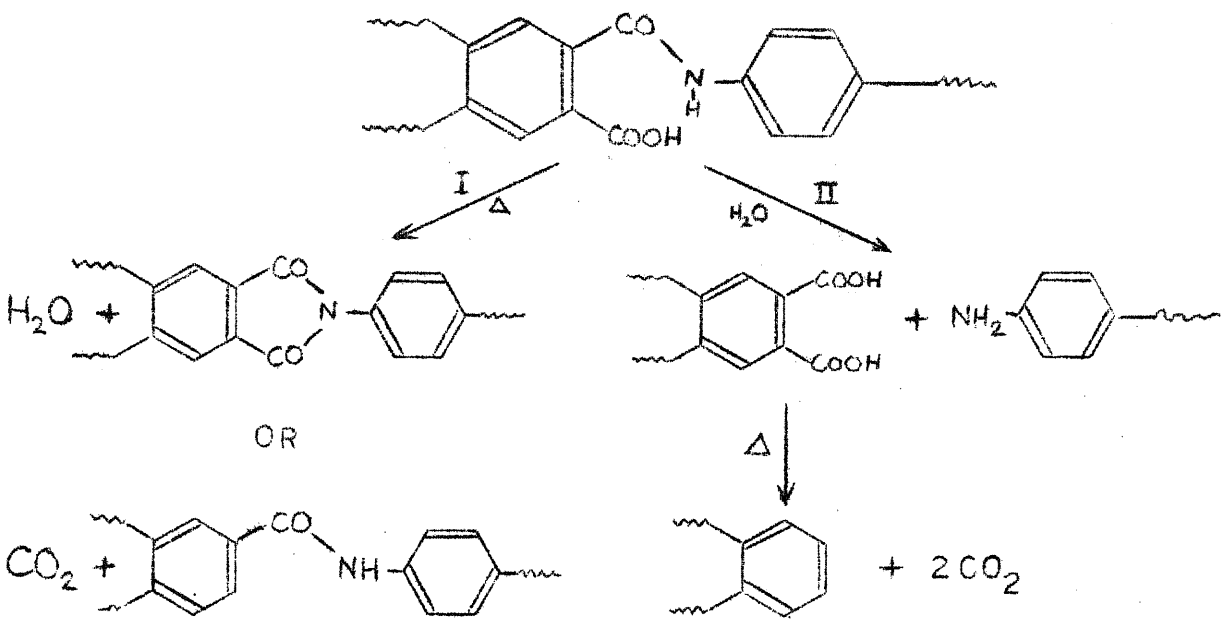
Values of CO/CO_2 for DDE/PMDA*

Moisture content	Pyrolysis temperature	CO/CO_2 (reproducible to within 5%)
Dried at 300°C immediately before use	600°C	1.66
	700°C	1.42
2-2.5% water-sample stored under normal atmospheric conditions.	600°C	1.50
	700°C	1.25
Saturated - stored in saturated atmosphere	700°C	0.79

Degradation mechanisms

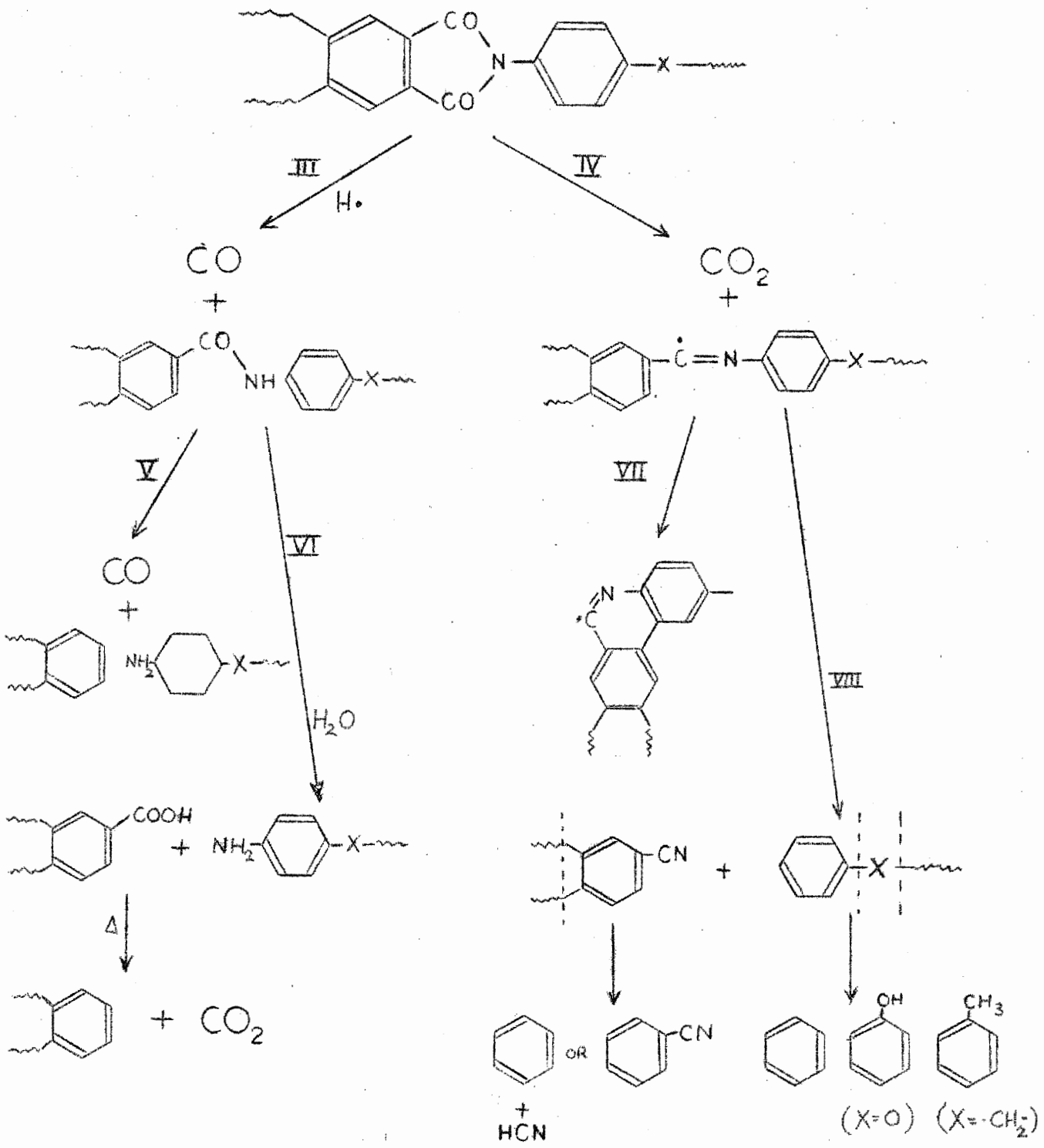
In view of these results it is clear that CO_2 does not originate from uncyclised units only.

Polyamic acid units may be expected to dehydrate or decarboxylate on heating (I), but when water is present hydrolytic scission followed by decarboxylation may occur (II):



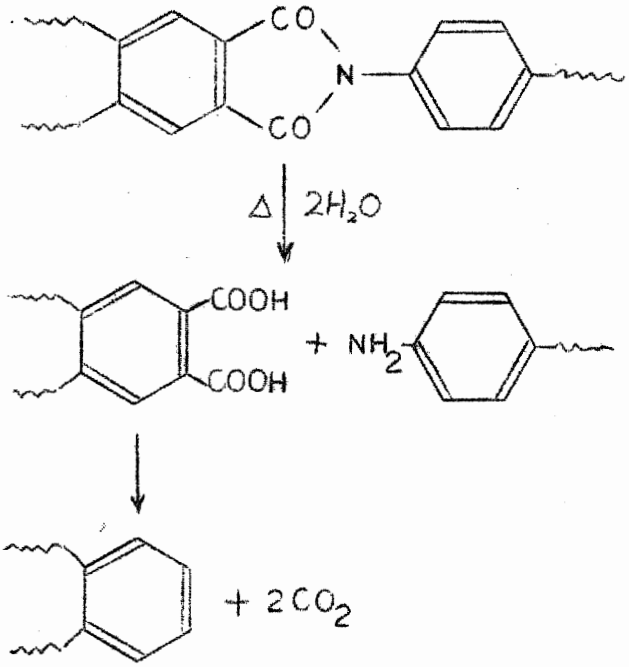
Assuming that all the imide carbonyl groups yield CO, and all the polyamic acid groups break down according to mechanism II, then $CO/CO_2 \simeq 15$ (1 polyamic acid group per eight polymer repeat units gives $2CO_2$ + 30 CO). Since the analysis of the chars indicated that a high percentage of the carbonyl groups were lost on pyrolysis, it must be concluded that the imide rings yield both CO and CO_2 when low CO/CO_2 ratios are recorded.

The following degradation mechanisms are suggested to explain the findings of the present work:


CO
N
X
CO
III
H•
IV
CO
+
CO2
+
CO
NH
X
C
N
X
V
VI
VII
CO
+
NH2
X
N
C
VIII
H2O
COOH
+
NH2
X
CN
+
X
Δ
+ CO2
CN
OR
+
HCN
OH
CH3
(X=O)
(X=-CH2-)

The variation in CO/CO_2 with pyrolysis temperature is accounted for if the relative contributions of mechanisms III and IV vary with temperature. This may well be the case because the removal of CO_2 probably requires a higher activation energy than the removal of CO and hence mechanism IV would tend to occur more readily at higher temperatures.

The increase in CO_2 yield with increasing moisture content of the polyimide may be attributed to mechanism VI and possibly to direct hydrolysis of the polyimide followed by decarboxylation:



The only degradation products found but not accounted for are hydrogen and methane. Hydrogen is stripped from aromatic nuclei at temperatures above 600°C (e.g. benzene $\xrightarrow{650°C}$ diphenyl + H_2), but the formation of methane is not easily explained.

References

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18. R.A. Dine-Hart, unpublished work.

List of Figures

Fig. No.

1. Aromatic polyimides

2. I/R spectrum of DDE/PMDA

3. I/R spectrum of DDM/PMDA

4. I/R spectrum of DBPh/PMDA

5. Gaseous degradation products of DDE/PMDA. Column: silica gel. Oven temp.: 50°C. Pyrolysis temp.: 700°C. Carrier gas: N_2, 40 ml/min.

6. Low boiling degradation products of DDE/PMDA. Column: 7,8 benzoquinoline/60-80 mesh Chromosorb P, 15/85. Oven temp.: 50°C. Pyrolysis temp.: 700°C. Carrier gas: N_2, 40 ml/min.

7. Higher boiling degradation products of DDE/PMDA Column: Apiezon L/60-80 mesh Chromosorb P, 10/90. Oven temp.: 150°C. Pyrolysis temp.: 700°C, Carrier gas: N_2, 40 ml/min.

8. I/R spectrum of DDE/PMDA tar

9. I/R spectrum of DDM/PMDA tar

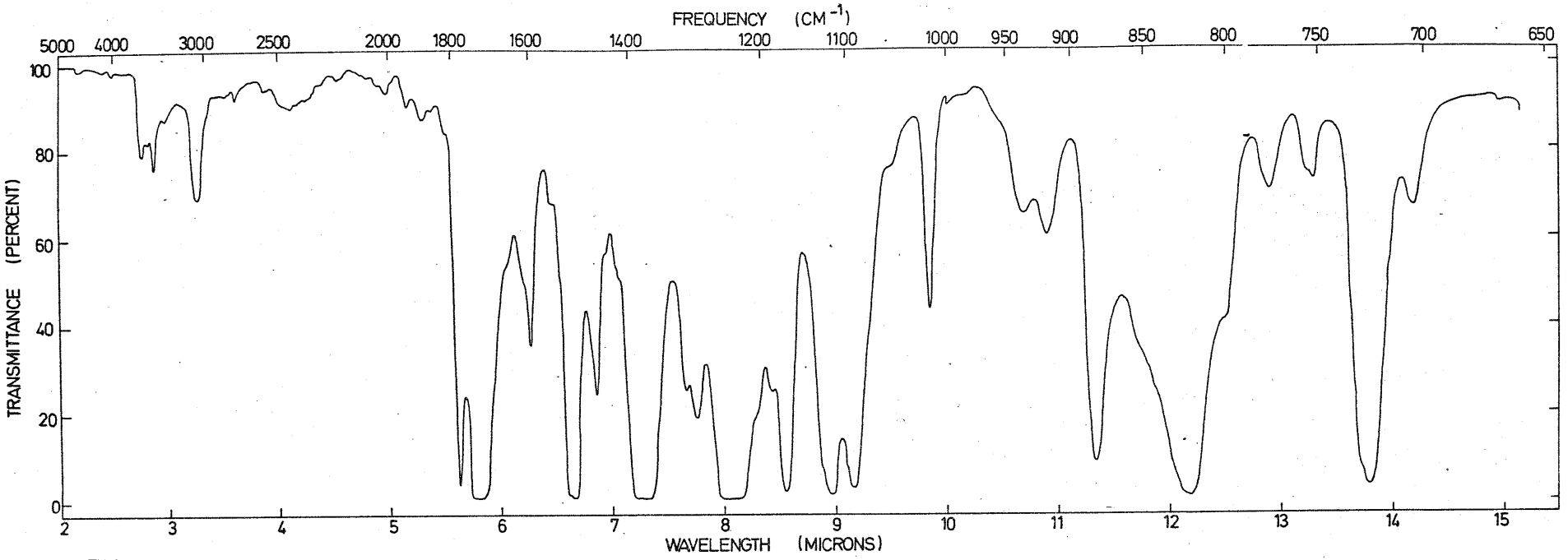
10. I/R spectrum of DBPL/PMDA tar.

11. I/R spectrum of DDE/PMDA char

12. Polyamic acid structure

13. I/R spectrum of DDE/PMDA between 2 and 5 microns.

14. Pyrogram and 'radiopyrogram' for DDE/PMDA*. Pyrolysis temp.: 700°C. Column: Silicon gel. Oven temp.: 50°C. Carrier gas: N_2, 40 ml/min.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TRANSMITTANCE (PERCENT)
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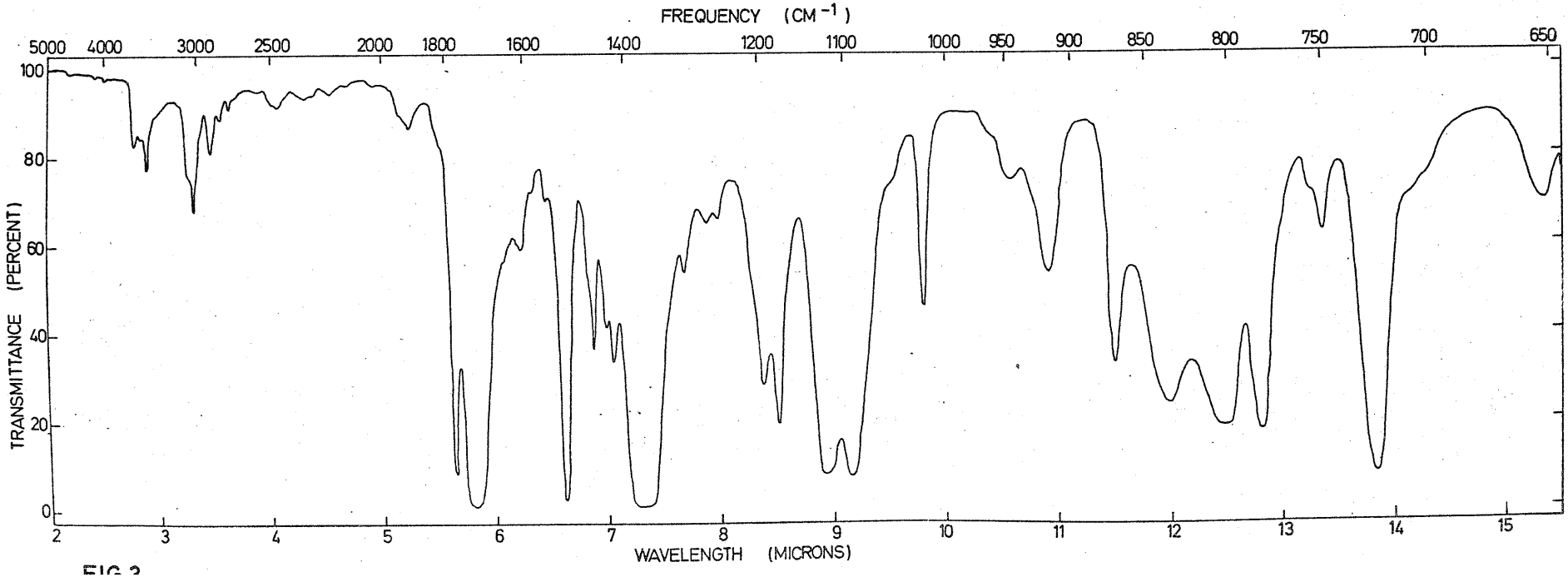
WAVELENGTH (MICRONS)

FIG. 2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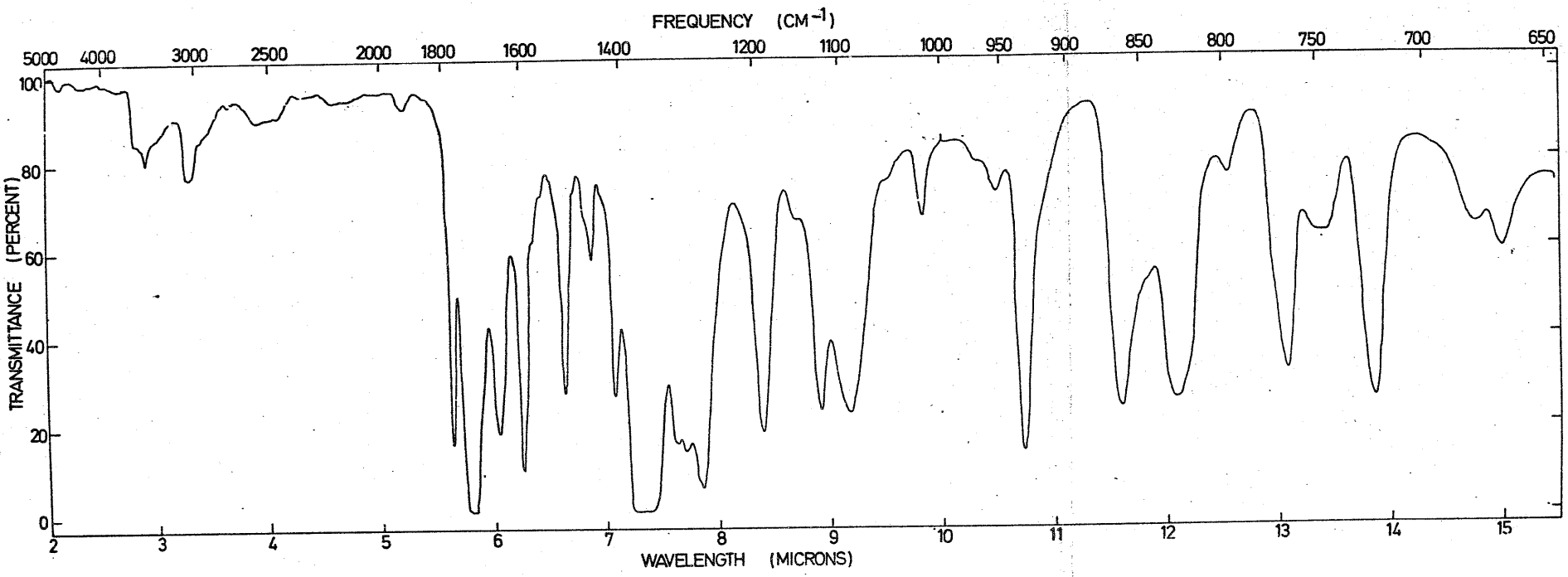
WAVELENGTH (MICRONS)

FIG. 3


FREQUENCY (CM^{-1})
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2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

FIG. 4

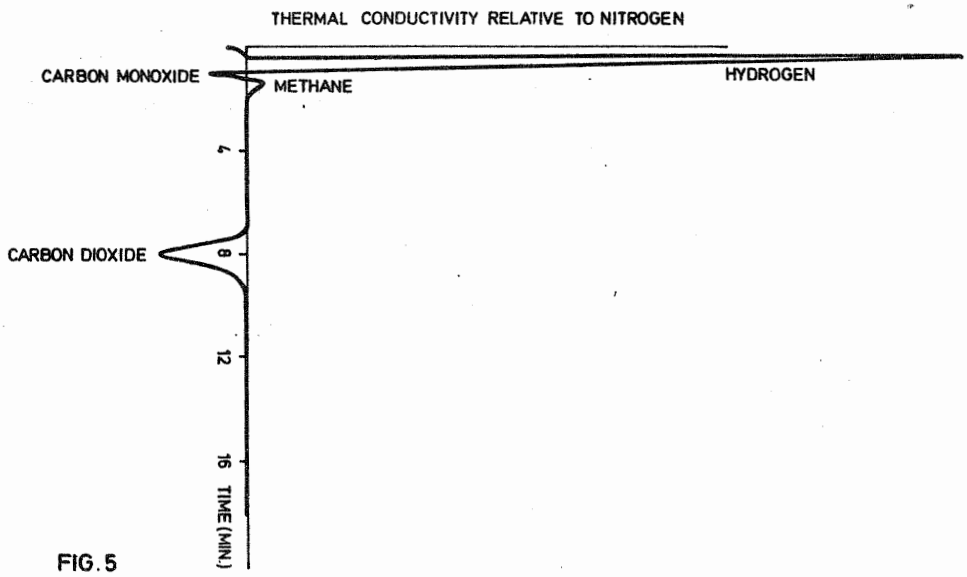

FIG. 5

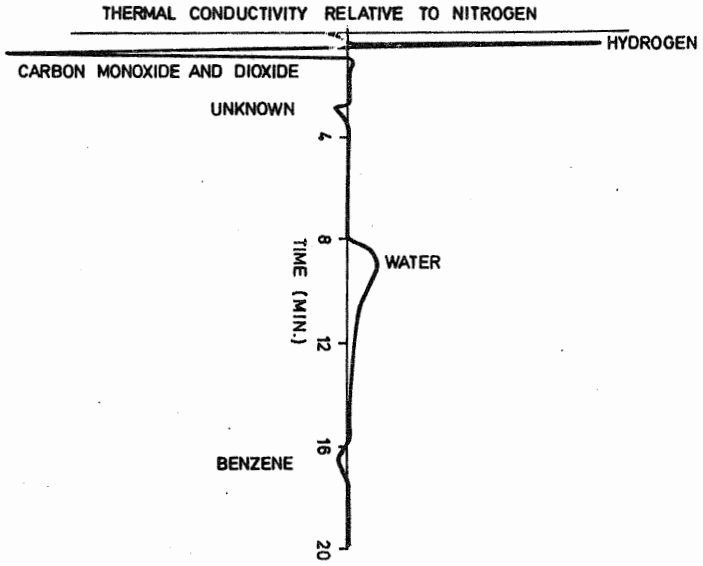

FIG. 6

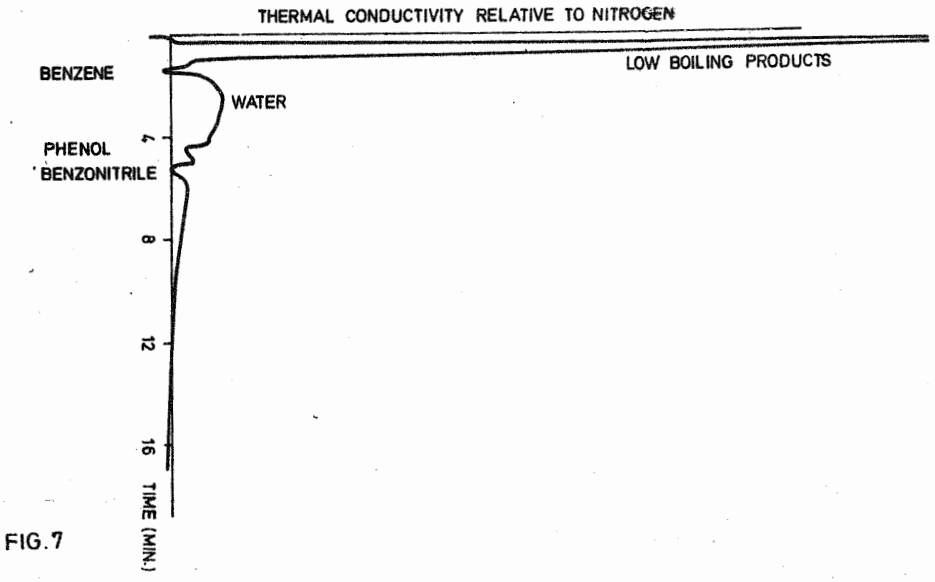

FIG. 7

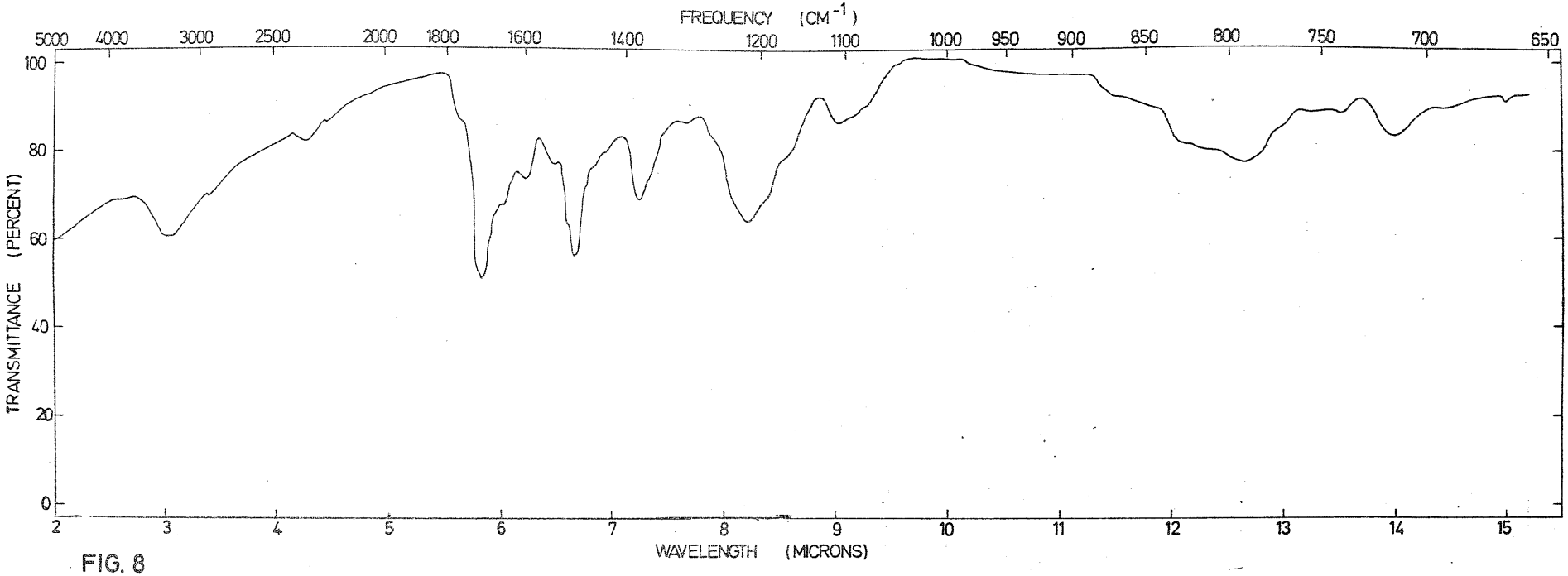
FREQUENCY (CM⁻¹)
5000 4000 3000 2500 2000 1800 1600 1400 1200 1100 1000 950 900 850 800 750 700 650
TRANSMITTANCE (PERCENT)
100 80 60 40 20 0
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

FIG. 8

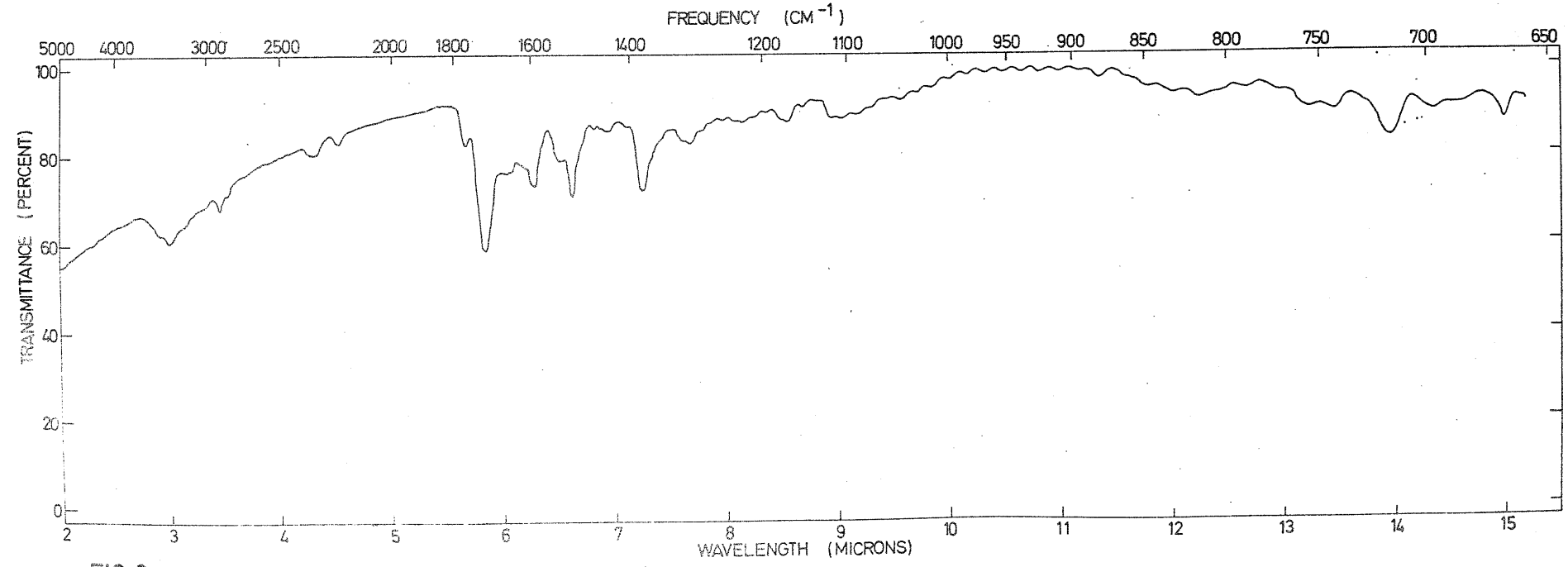
FREQUENCY (CM⁻¹)
5000 4000 3000 2500 2000 1800 1600 1400 1200 1100 1000 950 900 850 800 750 700 650
TRANSMITTANCE (PERCENT)
100 80 60 40 20 0
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

FIG. 9

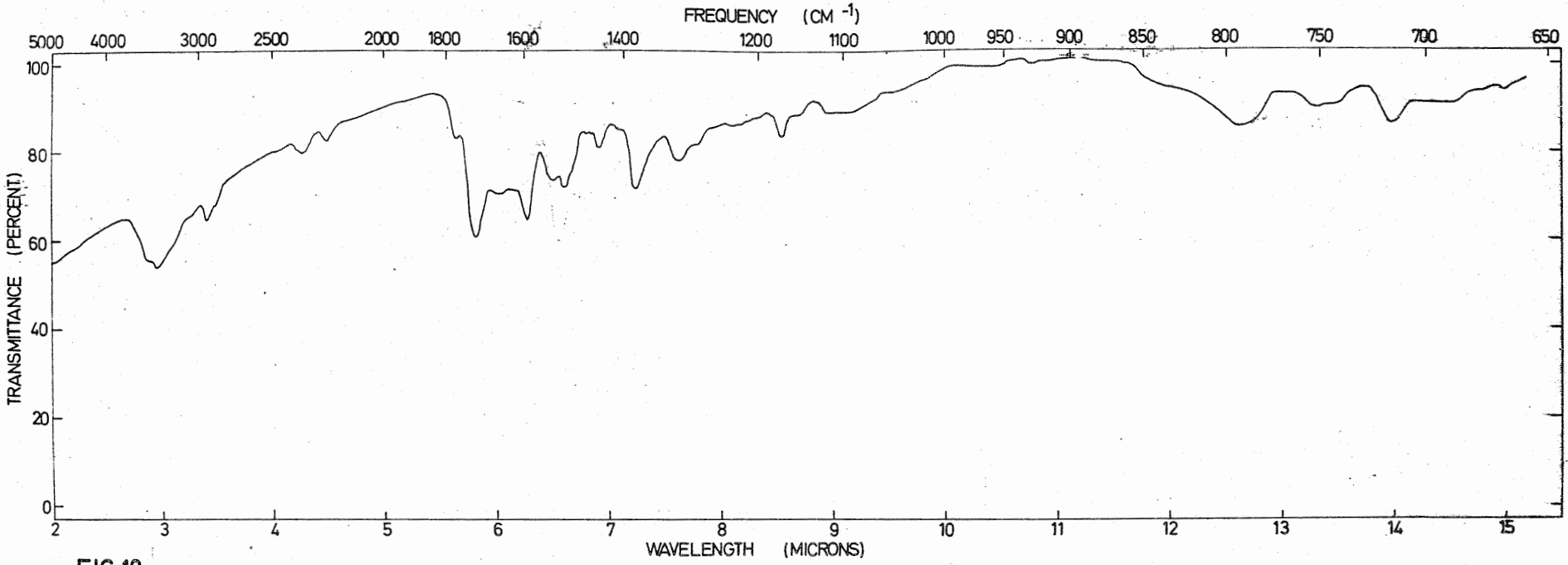
FREQUENCY (CM -1)
5000 4000 3000 2500 2000 1800 1600 1400 1200 1100 1000 950 900 850 800 750 700 650
TRANSMITTANCE (PERCENT)
100 80 60 40 20 0
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

FIG.10

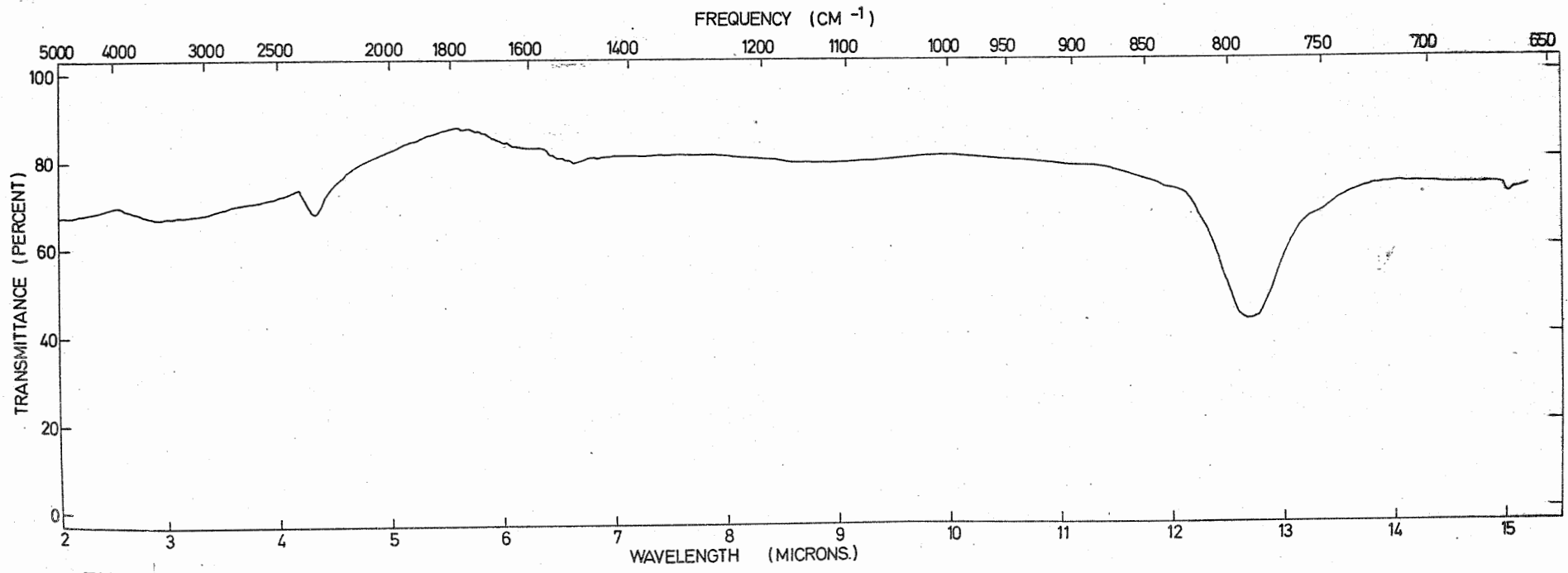
FREQUENCY (CM -1)
5000 4000 3000 2500 2000 1800 1600 1400 1200 1100 1000 950 900 850 800 750 700 650
TRANSMITTANCE (PERCENT)
100 80 60 40 20 0
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS.)

FIG.11

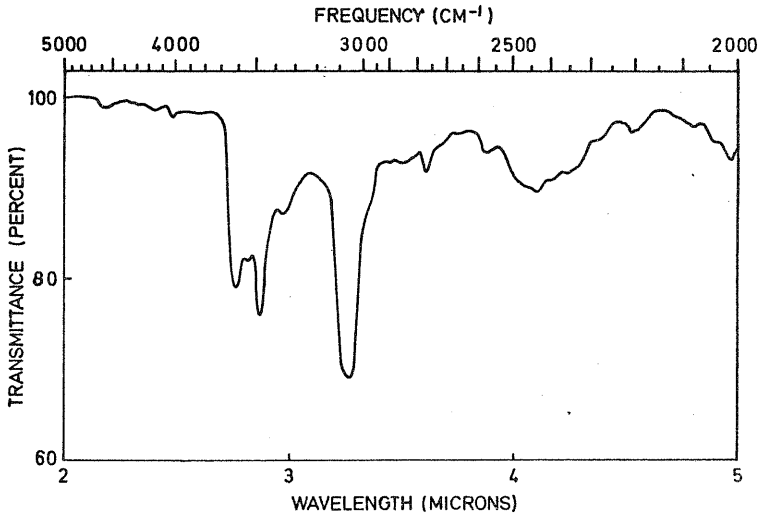
FREQUENCY (CM⁻¹)
5000
4000
3000
2500
2000
100
80
60
TRANSMITTANCE (PERCENT)
2
3
4
5
WAVELENGTH (MICRONS)

FIG.13

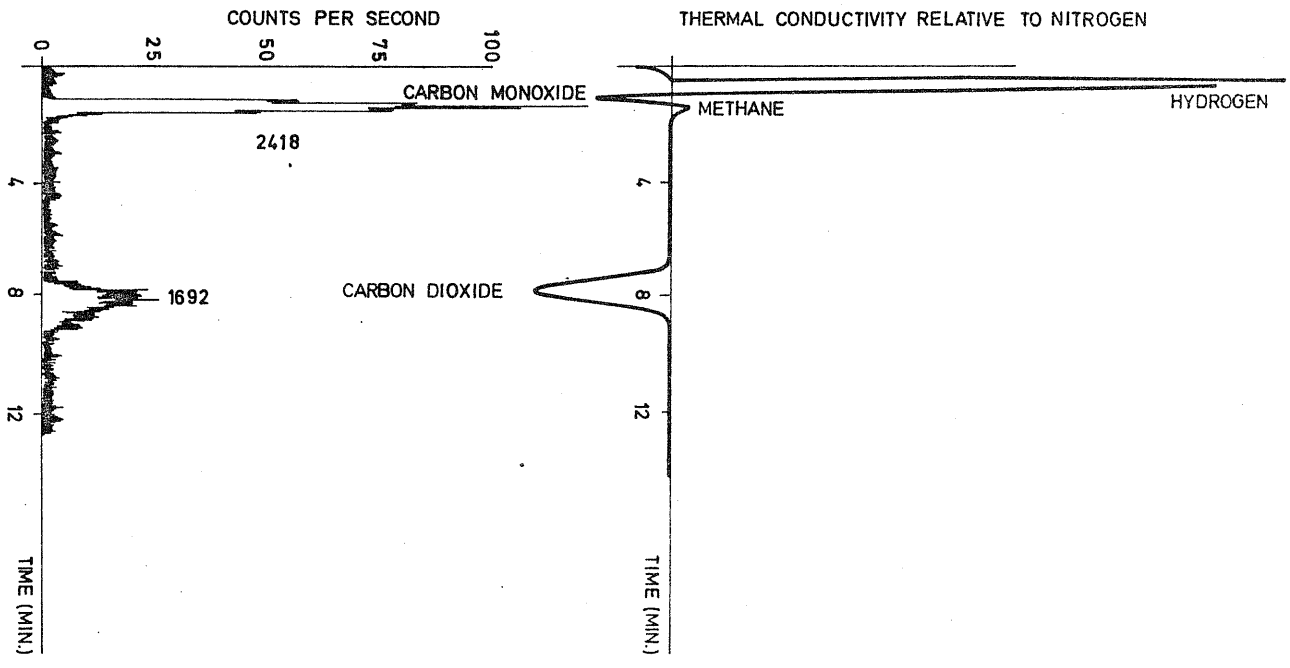
COUNTS PER SECOND
0
25
50
75
100
CARBON MONOXIDE
2418
1692
4
8
12
TIME (MIN.)
THERMAL CONDUCTIVITY RELATIVE TO NITROGEN
METHANE
HYDROGEN
CARBON DIOXIDE
4
8
12
TIME (MIN.)

FIG.14