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Gas chromatography and fragmentation-gas chromatography of diphosphine oxides and uranyl nitrate-diphosphine oxide complexes

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GAS CHROMATOGRAPHY AND FRAGMENTATION-GAS CHROMATOGRAPHY OF DIPHOSPHINE OXIDES AND URANYL NITRATE-DIPHOSPHINE OXIDE COMPLEXES

by

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INTRODUCTION

It is difficult to over-estimate the importance of gas chromatography among quantitative organic analytical tools. At its simplest, the technique may be used to quantitatively determine a large variety of compounds from major to trace concentrations whether occurring separately or in complex mixtures. Sample sizes required are extremely small. It is a convenient, rapid, accurate, and relatively inexpensive technique. With the availability of high, programmed, and sub-ambient temperature techniques and new column materials, the number of compounds capable of being quantitatively analyzed by gas chromatography is phenomenal.

Yet, with all of its attributes, gas chromatographic analysis suffers several serious limitations. While being a powerful quantitative analytical tool, conventional gas chromatography (g. c.) is a poor qualitative analytical tool. While being a technique of extremely great applicability, the vapor phase nature of the separation process limits its use to those species which can volatilize intact. Finally, and perhaps most important, gas chromatography has become an organic analytical tool with relatively little application to inorganic analytical problems. Great strides have been taken toward lessening each of these limitations.

The greatest publicized efforts of late have been those directed at applying g. c. to the analysis of metals. The

problem, here, has been to overcome the volatility limitation. It has long been known that many inorganic compounds or classes of compounds that can volatilize intact such as certain metal halides (56) and phosphorus halides (23) can be gas chromatographed. One approach to the gas chromatographic analysis of metals has been, then, to prepare volatile derivatives of the metals of interest and chromatograph the derivatives. A particularly elegant example of this concept is the recent work of Juvet and Fisher (56). These workers form the metal fluorides of molybdenum, tungsten, uranium, and ten other elements by means of a reactor in the carrier gas line of a gas chromatograph. The metal halides are swept out of the reactor as they are formed and onto an analytical column for separation.

The greatest hope of making g. c. a general inorganic analytical tool has come from reports of the gas chromatographability of metal complexes. Activity in this new field has been intense. Many publications concerning newly discovered chromatographable complexes and improvements in many aspects of the gas chromatography of complexes appear each year (41,92). Moshier and Sievers, pioneers in the field, have published a book on the topic (76).

The success of these approaches demonstrates the scope of conventional gas chromatography. Although representing a very significant practical advance for gas chromatographic analysis, these approaches do little more, basically, than add

to the list of gas chromatographable molecules. Both the complex and reaction techniques operate within the framework of significant volatility.

The greatest steps toward circumventing the volatility requirement and at the same time making g. c. a useful qualitative analytical tool have come as a result of the introduction of "pyrolysis-gas chromatography" (74). The principle of the technique is very simple. The sample is thermally degraded in the carrier gas line and the degradation products separated by gas chromatography.

The chromatogram of the degradation products, the fragmentation pattern, should be characteristic of the molecule degraded. A given compound would be expected to yield a large number of degradation products, and consequently, a large number of peaks would be expected to appear in the fragmentation pattern. The positions and relative sizes of these peaks could be used for identification of the sample with much greater confidence than a single retention parameter as would be obtained if the sample were analyzed by conventional gas chromatography.

Assuming reproducible operating conditions, it would be expected that the size of the peaks in the pattern would be related to the size of the sample degraded. As such, fragmentation-gas chromatography should be applicable to quantitative as well as qualitative analysis.

Most importantly, volatility of the sample is no longer

required. Theoretically, with this extension, any compound that yields, upon thermal degradation, organic or inorganic products which can be gas chromatographed at column temperatures up to 350°C can be identified and quantitatively determined with little more than a basic gas chromatograph.

Because the primary difficulty in applying gas chromatography to the analysis of metals is finding metal-containing compounds of sufficient volatility, it seemed that fragmentation-gas chromatography, having no volatility requirement, might be advantageously applied to the problem. A search of the literature revealed that the potential of fragmentation-gas chromatography as an inorganic analytical tool had not been evaluated.

One means of applying the technique to the analysis of metals might involve the fragmentation of metallo-organic compounds followed by the gas chromatographic analysis of the organic breakdown products. In the simplest case, a solution of a metal-ligand complex containing no excess ligand, a given volume of solution could be deposited in the fragmentation chamber, the solvent evaporated and the resulting solid metal-ligand complex fragmented. The size of the peaks or any given peak in the fragmentation pattern would be expected to be proportional to the total amount of sample fragmented. The size of the peak(s) could be related to the weight of sample which is in turn related to the weight of metal present. Knowing the volume of solution subjected to analysis would

allow the calculation of its metal concentration.

This is, of course, an extremely artificial example. The absence of excess ligand requires that the metal content be known before analysis. Nevertheless, the analytical procedure would be valid. The analysis could be carried out by extracting the metal into an organic phase, depositing a known volume of the extract in the fragmentation chamber, vaporizing the solvent and fragmenting the residue. The presence of excess ligand, as would be expected for any practical analytical scheme, simply imposes an additional requirement. The fragmentation pattern must be sensitive to complexed ligand in some way.

The ideal situation would yield a fragmentation pattern containing breakdown products characteristic of complexed ligand and those characteristic of uncomplexed ligand. Under these circumstances a peak corresponding to complexed ligand (a "complex-sensitive" peak) could be used as a measure of the amount of metal present in the sample. The presence of excess ligand would be of no concern because the uncomplexed ligand would not contribute to the size of the peak monitored. Equally ideal would be the case allowing selective degradation of the metal-ligand complex while leaving uncomplexed ligand intact.

Fragmentation-g. c. techniques should be applicable to inorganic analysis under conditions other than the ideal. For example, although selective degradation of complex might not

be possible, a selective volatilization of excess ligand might be possible. In this case, excess ligand can be removed along with the solvent leaving only complexed ligand for fragmentation. Actually, it is not essential that the entire fragmentation pattern or any part of it arise from complexed ligand alone. It is essential, however, that some aspect of the pattern be "complex-sensitive".

It was felt that a system suitable to evaluate the potential of fragmentation-gas chromatography as an inorganic analytical tool should meet several requirements. It was felt that the ligand should be a proven solvent extractant so that any success with fragmentation-chromatographic analysis could be translated into a workable analytical technique. A ligand yielding a simple fragmentation pattern was desired to simplify data interpretation. Because complexes are often altered by heat, the sample would have to be maintained at a relatively low temperature prior to controlled fragmentation which, with the assembly available for these studies, limits the size of the fragments capable of reaching the analytical column. As a result, an additional requirement was that a significant number of low-boiling fragments be formed on fragmentation. Finally, it was felt that an ideal system would be one in which the functionality involved in complexation was also involved in the degradation mechanism of uncomplexed ligand because this would increase the probability of complexation directing the formation of a complex-sensitive

peak.

The diphosphine oxides of the following type appear to

$$(R)_2\overset{\uparrow}{O}P(CH_2)_n\overset{\uparrow}{O}P(R)_2 \quad (n = 1,2,3,4)$$

meet all of the stated requirements. They are proven solvent extractants (77,78,85). Work on monophosphine oxides (5) indicated that a significant yet simple fragmentation pattern of low-boiling hydrocarbons might be obtained on breakdown of the diphosphine oxides. Very importantly, this same work resulted in strong indications that the phosphoryl oxygens were involved in the degradation mechanism of the monophosphine oxides.

Because they met the assumed requirements, the diphosphine oxides were chosen as the complexing agent to evaluate the potential of fragmentation-g. c. as an inorganic analytical tool. Because the diphosphine oxides were known to be most useful for the extraction of the uranyl ion and that it is possible to prepare solid uranyl nitrate-diphosphine oxide complexes, uranium, as uranyl nitrate, was chosen as the complexed metal for this investigation.

Selection of the diphosphine oxides presents an additional problem in any study where the overall fragmentation pattern is of interest. In order to guarantee that any high-boiling organophosphorus breakdown products that might be formed reach the analytical column, it is necessary to maintain the fragmentation assembly at a relatively high temperature (approximately 300°C) prior to and after fragmentation.

At elevated temperatures a portion of the sample might be volatilized prior to fragmentation and eventually be deposited on the analytical column. Similarly, undegraded diphosphine oxide released during the fragmentation process might eventually find its way to the column.

If the intact diphosphine oxides are gas chromatographable, the fragmentation patterns will contain a peak corresponding to the diphosphine oxide which could easily be misconstrued as a fragmentation product. The diphosphine oxides may be partially chromatographable in that their chromatography is attended by some degree of thermal decomposition in the inlet or on the column. In this case, the fragmentation pattern will contain a poorly shaped peak for undegraded diphosphine oxide characteristic of column-induced degradation and peaks characteristic of inlet-induced decomposition. In either case, the result is an easily misinterpreted fragmentation pattern.

An additional danger is that impurities in the diphosphine oxides might also reach the analytical column in a manner analogous to the undecomposed diphosphine oxide. The presence of peaks corresponding to these impurities would further complicate interpretation of the fragmentation patterns.

A search of the literature revealed that no work on the gas chromatographic analysis of diphosphine oxides had been reported. As a result, a study of the behavior of these compounds under gas chromatographic conditions was a necessary

prerequisite to their use in the fragmentation studies.

It was then noted that whereas the diphosphine oxides were becoming important analytical reagents, little has been reported on their analysis. A titrimetric method (84) has been reported but is attended by several difficulties and is not generally applicable. The only other method reported is a spectrophotometric procedure for the determination of the diphosphine oxides in aqueous solutions (82). These findings suggested that a study of the fragmentation-gas chromatography of the diphosphine oxides could yield a needed method for the quantitative determination of these compounds in addition to aiding in the evaluation of fragmentation-g. c. as an inorganic analytical tool.

In the course of this investigation, it was found that judicious selection of chromatographic conditions allowed all of the diphosphine oxides available for study to be gas chromatographed intact. As a result, this thesis is presented in two parts. Part I is concerned with the conventional gas chromatography of the diphosphine oxides with particular interest in the behavior of these compounds under chromatographic conditions and the application of the technique to their quantitative determination. Part II deals with the application of fragmentation-gas chromatography to the diphosphine oxides and their corresponding uranyl nitrate complexes with particular interest in obtaining some measure of the potential of fragmentation-gas chromatography as an inorganic analytical tool.

PART I. GAS CHROMATOGRAPHY OF DIPHOSPHINE OXIDES

REVIEW OF THE LITERATURE

Among the earliest reported separations of organophosphorus compounds is the separation of triethyl, triphenyl, and tris(m-tolyl) phosphate developed during an investigation of the analysis of plasticizers (68). The majority of the publications dealing with the gas chromatography of organophosphorus compounds (Table 1) have, however, resulted as support efforts for studies of various aspects of organophosphorus chemistry.

DeRose, Gerrad, and Mooney (29) present a method for the gas chromatographic analysis of six dialkyl hydrogen phosphites developed during an investigation of ester-interchange in this class of compounds. Feinland, Sass, and Buckler (39) established conditions for the separation of all of the possible oxidation products of two organic phosphines. During a study of the photochemical phenylation of tri-n-butyl phosphite, Plumb and Griffin (90) used g. c. to aid in the identification of the unexpected product tri-n-butyl phosphate and to monitor products of photo-initiated air oxidation of several lower trialkylphosphites. Walling (111) used gas chromatography to identify and estimate products of reactions of thiol and alkoxy radicals with trialkylphosphites. Denney and Boskin (24) investigated the reaction of tributylphosphines with episulfides by monitoring the butene generated. Sauers and Landesberg (95) identified products of a rearrange-

Table 1. Organophosphorus compounds for which conditions are available for gas chromatographic analysis

Class	Reference
Alkyl and aryl phosphates	68
Alkyl hydrogen phosphites	29,97
Aryl phosphines and phosphine oxides	43
Alkyl phosphites and phosphonyl esters	23
Alkyl phosphates and phosphites	90
Alkyl phosphines, phosphites, phosphine oxides, phosphonates, phosphates, and phosphinates	39
Alkyl and aryl phosphine oxides, phosphine sulfides, phosphinates, phosphonates, phosphates, phosphinic acids, phosphorylated amidines, phosphines, and phosphites	11
Alkyl phosphates	58[a]
Alkyl and aryl phosphorothioates	113
Alkyl phosphates and organophosphorus pesticides	16[a]
Organophosphorus pesticides	18[a],106
Organophosphorus insecticides	12

[a]Denotes paper dealing primarily with selective phosphorus detection.

ment during phosphoryl chloride-pyridine dehydration.

General conclusions concerning the gas chromatographability of organophosphorus compounds awaited more thorough consideration of the analytical technique. Shipotofsky and Moser (97), although primarily interested in the g. c. of inorganic phosphorus-containing compounds, reported the separation of dimethyl and diethylphosphate by columns of di-n-butyl pthalate and Apiezon K. These authors reported the necessity of using Fluoropak 80 as solid support claiming that Chromosorb produced severe tailing.

At about the same time, Gudzinowicz and Campbell (43) reported that the quantitative analysis of a variety of aryl phosphines and phosphine oxides was possible by gas chromatography with virtually no special precautions. A common silicone liquid phase (SE-30) impregnated on Chromosorb W and packed in stainless steel tubing was found to be a perfectly satisfactory column. The flash heater was maintained at 405°C without evidence of decomposition. Using a simple 240-340°C temperature program allowed the resolution of triphenylphosphine, p-methoxyphenyl diphenylphosphine, di(p-methoxyphenyl) phenylphosphine, p-methoxyphenyl diphenylphosphine oxide, tri(p-methoxyphenyl) phosphine, and tri(p-methoxyphenyl) phosphine oxide from one another in a single run.

A review (23) on the gas chromatography of organophosphorus compounds supported the contention that simple silicone liquid phases are widely applicable to the separation of these

compounds. Further defining the requirements for a system capable of general application to the gas chromatography of organophosphorus compounds, the authors stated that care must be taken to avoid allowing water to enter the system and that glass columns and on-column injection are often required for quantitative analytical purposes. They further pointed out the advantage of using silanized supports and urged the use of programmed temperature techniques for the separation of mixtures containing a large variety of organophosphorus compounds.

Berlin et al. (11) published the results of a four-year study of columns applicable to the g. c. of organophosphorus compounds and described the use of dimethyldichlorosilane-treated Chromosorb G as a solid support. Twenty-eight compounds representing eleven classes of organophosphorus compounds were gas chromatographed using a flame ionization detector with the conclusion that whereas silicone liquid phases are quite generally applicable,due to the polar nature and high-boiling characteristics of organophosphorus compounds, considerable care must be exercised in choosing a column for a particular separation.

The more complicated organophosphorus compounds used as pesticides and insecticides have been found to be somewhat more sensitive to heat than most of the simpler organophosphorus compounds (47). As a result, the use of neopentylglycol succinate and phenyl diethanolamine have been suggested as preferred liquid phases (47). In at least one publication

(106) it is claimed that diethyleneglycol succinate is the most generally applicable liquid phase for pesticide analysis. Regardless of the reported complications involved in using silicone liquid phases for pesticide analysis, a large degree of success has been reported with their use (12,18,106).

An advance in the chromatographic analysis of organophosphorus compounds as important as any other is that resulting from the development of phosphorus-selective detectors. Karmen (58) described a phosphorus-halogen-specific flame ionization detector. Burchfield, Rhoades, and Wheeler (18) introduced a microcoulometric detector sensitive to only phosphorus, sulfur, and halogens. At least one paper has appeared on the application of flame photometric detectors to selective phosphorus detection (16). McCormack, Tong, and Cooke described an emission detector, based on microwave excitation, capable of being phosphorus-selective (73). The use of any of these detection systems results in greatly simplified chromatographic conditions and sample preparation.

Gas chromatography has become an effective analytical tool for the quantitative determination of organophosphorus compounds. Its use in aiding in the identification of organophosphorus compounds has been demonstrated repeatedly. The reported (3) use of tri-n-butyl phosphate as stationary phase for the study of diluent effects in solvent extraction further demonstrates the value of gas chromatography to organophosphorus chemistry.

EQUIPMENT, MATERIALS AND PROCEDURES

Equipment

All of the gas chromatograms were obtained with a Beckman GC-4 model gas chromatograph equipped with thermal conductivity and dual hydrogen flame ionization detectors, flash vaporization and on-column injection ports, programmed column temperature module, and electrical discharge pyrolysis-gas chromatography capability. Injection of samples was by Hamilton micro-syringe. A Bristol model 560 Dynamaster recorder was used to record the chromatograms. Peak areas were determined with the aid of a Disc Integrator.

Column preparation was aided by vibration of packed columns with Burgess Vibro-gravers.

Infrared spectra were obtained with a Perkin-Elmer model 21 Infrared Spectrophotometer.

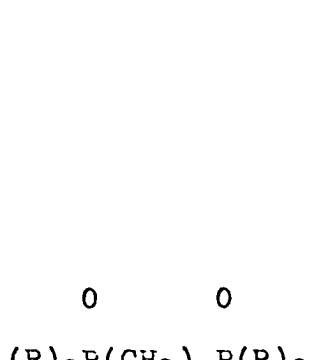
Materials

The diphosphine oxides (Table 2) were obtained from laboratory stock and used without additional treatment. The preparation and properties of these compounds have been described (77,78,85,94).

The uranyl nitrate-diphosphine oxide complexes were obtained by mixing equimolar amounts of uranyl nitrate and diphosphine oxide in n-propanol and filtering the precipitate. The complexes were recrystallized from n-propanol.

The identities of the uranyl nitrate complexes MHDPO-U,

Table 2. Nomenclature and structures of the diphosphine oxides

Structure R	n	Abbreviation	Name
	1	MNDPO	Methylene-bis(di-neohexyl phosphine oxide)
	1	MEBDPO	Methylene-bis(di-2-ethylbutyl phosphine oxide)
	1	MEHDPO	Methylene-bis(di-2-ethylhexyl phosphine oxide)
	1	MHDPO	Methylene-bis(di-n-hexyl phosphine oxide)
	2	EHDPO	Ethylene-bis(di-n-hexyl phosphine oxide)
	3	PHDPO	Propylene-bis(di-n-hexyl phosphine oxide)
	4	BHDPO	Butylene-bis(di-n-hexyl phosphine oxide)

EHDPO-U, PHDPO-U, and BHDPO-U were confirmed by comparison of their infrared spectra with standard spectra. The expected shifts in the phosphoryl band positions were noted in MEBDPO-U, MEHDPO-U, and MNDPO-U spectra and taken as evidence of complex formation.

The extent of complexation (= 90% for each) was assayed by comparison of the sizes of complexed and uncomplexed phosphoryl bands, and noting the size of the diphosphine oxide peak obtained on injection of solutions of the various uranyl nitrate complexes into the gas chromatograph. Such an assay was found sufficient for these studies.

Cis,trans-pentene-2 (mixed isomers), hexene-1, and n-heptane were obtained from Phillips Petroleum Co. Tribenzyl amine and neocuproine were obtained from Eastman Organic Chemicals.

Stock helium was used as the carrier gas for all of the studies employing thermal conductivity detection. High-purity (Zero-gas) helium was used for studies involving flame detection. The high-purity carrier gas and "Zero-gas" hydrogen and air for flame detector operation were obtained from Matheson Company, Incorporated.

Liquid partitioning agents and solid supports were obtained from Applied Science Laboratories. Stainless steel and copper tubing was obtained from laboratory stock and flushed with acetone before use. Glass tubing was obtained from Fred S. Hickey Corp., Shiller Park, Illinois. Swagelock

fittings were obtained from Hawkeye Valve and Fitting Company, Des Moines, Iowa.

The columns used in these studies are given in Table 3. In each case, the solid support is 100/120 mesh. The column preparation procedure is described in the following section.

Procedures

Column preparation

It is necessary to elaborate on the method used for column preparation because it involves a new support coating technique.

Many procedures are recommended for coating solid supports prior to packing analytical columns (49,83,99) and after packing columns with uncoated support (4,15). Coating a support after it has been packed (in-place coating) is said to result in reproducible columns (4) but has the definite disadvantage that only enough packing is made to fill the single column. In this thesis work, it was desired to prepare a large enough batch of packing material to pack several columns of different characteristics such that the influence of these characteristics could be studied without danger of irreproducible packings complicating the results. Thus, a "prepacking" method of support-coating was of greater interest.

Three significantly different techniques were noted for the coating of supports prior to packing; the classical method (49,99), a frontal analysis technique (99), and a procedure

Table 3. Types of columns used in this study of the gas chromatography of the diphosphine oxides

Column	Number
4 ft., 0.25 inch o.d., 5% SE-30/DMCS-Chromosorb G (glass)	1
4 ft., 0.25 inch o.d., 5% SE-30/DMCS-Chromosorb G (copper)	2
4 ft., 0.25 inch o.d., 10% SE-30/DMCS-Chromosorb W(glass)	3
4 ft., 0.25 inch o.d., 10% SE-30/HMDS-Chromosorb W(glass)	4
4 ft., 0.25 inch o.d., 10% SE-30/Celite (glass)	5
4 ft., 0.25 inch o.d., 5% Apiezon N/DMCS-Chromosorb G(glass)	6
4 ft., 0.25 inch o.d., 5% SE-52/DMCS-Chromosorb G (glass)	7
4 ft., 0.25 inch o.d., 0.5% SE-52/silicone treated glass beads (glass)	8
4 ft., 0.125 inch o.d., 5% SE-30/DMCS-Chromosorb G(glass)	9
1.5 ft., 0.125 inch o.d., 5% SE-30/DMCS-Chromosorb G(glass)	10
8 ft., 0.25 inch o.d., 5% SE-30/DMCS-Chromosorb G (glass)	11

involving the suction of the liquid phase solution through the support (83). It was found, as has been previously pointed out (99), that the classical method results in poor liquid phase distribution. Tests also showed that whereas the frontal analysis technique improved the distribution, coating uniformity remained less than desired. The suction technique seemed to yield a more uniform coating but required the use of large amounts of liquid phase. The technique developed at this Laboratory takes advantage of the frontal analysis procedure for coating the support and the drying procedure used by the workers presenting the suction procedure of packing preparation.

In the technique used here, a solution of the liquid phase in a suitable solvent (one being volatile and capable of dissolving the liquid phase) is passed through the solid support contained in a cylindrical vessel (much like a liquid chromatography column but approximately three inches in diameter) tapered to form a spout at one end and plugged with glass wool (or containing a glass frit). When solution stops emerging from the bottom of the column, the column is tapped to insure the absence of excess solution in the damp support. The solvent is then removed by heating the vessel with heat lamps (two) while passing purified air up through the bottom of the column.

Because support materials used in gas chromatography are only slightly adsorptive, the chances of chromatographic

fractionation of the liquid phase on passage through the support bed are very small (99). To insure the absence of fractionation, it is suggested that two wetting volumes (the volume of solvent required to just wet the support) be passed through the support.

Knowledge of wetting volumes allows the calculation of the liquid phase concentration required in the solution to produce a desired percentage coating. It has been found that it is possible to predict and reproduce percentage coatings at least as well as is possible with the classical coating procedure. More important, coating uniformity is much better (Table 4) than obtained with the classical procedure and is also improved over the reported frontal analysis technique.

Table 4. Comparison of the uniformity of liquid phase coating obtained from the classical and "new" support-coating techniques

Mesh	Weight of coated support (gm.)		Percentage coating (%)	
	Classical	New	Classical	New
20	0.08	0.32	37.4	29.8
40	0.61	0.24	35.2	23.8
60	1.05	0.21	28.7	23.3
80	19.87	1.68	16.5	19.2
100	24.87	35.83	14.0	16.0
>100	0.60	2.13	12.6	14.9

After drying, the coated support is poured from the vessel and sieved to remove any particles large enough to complicate packing. The sieved material is then packed into glass or metal tubing.

Chromatographic studies

All of the columns of Table 3 were used to assess the general chromatographic behavior of the diphosphine oxides. Generally, 5.0 to 10.0 μl. of 0.05 M solutions of the samples in 1,2-dichlorobenzene or 1,2-dichloroethane were injected. In all studies, the retention positions were measured with an engineering rule calibrated in 40 units to the inch. Measurements were made from the air peak when thermal conductivity detection was employed and from injection for ionization detection studies. Peak areas, given in disc units (1/100 of one sweep of the integrator pen) times detector attenuation, were determined with a Disc Integrator.

Collections for infrared studies were carried out by allowing the effluent from the thermal conductivity detector corresponding to the diphosphine oxide peak to condense in a small mortar. For smaller amounts of sample, the effluent was allowed to condense on small KBr windows.

The chromatograms of Figures 1 and 2 were obtained for 5.0-μl. samples of 0.05 M solute using column 1 (Table 3) at a temperature of 290°C, an inlet temperature of 320°C, and a carrier gas flow rate of 150 ml./min. The data from this column were used for the adjusted retention correlations (Figures 6 and 7).

Column 1 (Table 3) was used to obtain the chromatogram for MNDPO (Figure 3) by programming the column temperature from 120 to 280°C for 13 minutes. The size of the sample was

5.0 µl. of 0.05 M MNDPO. Column number nine yielded the separation in Figure 4 at a temperature of 280°C and flow rate of 22 ml./min., with the injection of a solution containing 5.1, 11.3, 14.7, 4.1, and 5.3 µg. of MNDPO, MHDPO, EHDPO, PHDPO, and BHDPO respectively. MEBDPO and MEHDPO were run separately under identical conditions and their peak positions superimposed on the above chromatogram.

Adsorption studies were carried out using column number one at a temperature of 285°C, flow rate of 130 ml./min., and an inlet temperature of 300°C. High column temperature, inlet-induced decomposition studies were carried out with column seven at a 140 ml./min. carrier gas flow rate and a column temperature of 285°C. Low column temperature studies were carried out at ambient temperature with column-type seven. Programmed temperature studies were carried out using column number one. Column number ten, operated at a carrier gas flow rate of 22 ml./min. and column temperatures of 270 and 290°C for MNDPO and EHDPO respectively, was used to obtain the quantitative analytical data of Table 8. Response factors were obtained using the same column and flow rate as used for the MNDPO and EHDPO analyses but at a column temperature of 280°C.

INVESTIGATIONS AND RESULTS

Conditions have been established for the gas chromatographic separation of the diphosphine oxides. Chromatograms show that excellent peak shapes and good separations can be expected. In general, conditions for chromatographing the diphosphine oxides differ little from those applicable to most high-boiling compounds.

Gas Chromatographic Conditions

Liquid phase

The necessity of operating at high column temperatures limits the choice of liquid partitioning agent to the silicones, some Apiezons and several more selective phases such as polysulfone and Versamid. Because the diphosphine oxides have significantly different boiling points it could be expected that a simple "boiling point" liquid phase would show sufficient selectivity to allow their separation. This expectation is borne out.

The majority of the work described in this thesis was carried out using the methyl silicone SE-30 or the methyl phenyl silicone SE-52 as the liquid phase. No significant differences in separating ability was noted for these silicones.

Several Apiezons were also tested but ruled out as useful for the separation of the diphosphine oxides because of

significant column bleeding. In addition, peak shape was generally broad making baseline resolution difficult.

Solid support

The choice of solid support was found to be very important to the success of these studies. Untreated diatomaceous earths coated with five to ten percent silicone liquid phase always resulted in significant tailing of the peaks and in relatively broad peaks. Greater success was realized using any silanized support presumably because of decreased support adsorption of the sample.

Whereas Chromosorb W treated with either hexamethyldisilazane (HMDS) or dimethyldichlorosilane (DMCS) greatly improved the peak shapes, the DMCS-treated support was found to be somewhat superior. In agreement with other workers (11), the use of DMCS-treated Chromosorb G resulted in peaks of greater symmetry than either of the above columns containing Chromosorb W.

Silanized glass beads were also investigated as a potential support because sample adsorption would be expected to be less than with a silanized diatomaceous earth. Columns of 0.5% SE-30 on 60/80 mesh beads were found to result in skewed peaks for the diphosphine oxides. The low capacity of glass bead columns indicates that the peak asymmetry is associated with column overloading. Greater column bleeding was also noted.

Construction materials

It was found absolutely essential to employ an all-glass system in the analysis of the diphosphine oxides. The use of copper columns always resulted in a relatively sharp peak superimposed on a broad, hump-like, trace. Such a peak shape is a strong indication of column-induced thermal decomposition of the sample. Similar behavior was noted with stainless steel columns.

It is also essential that the inlet be glass-lined. Without the liner, peaks in addition to those corresponding to either the sample or impurities in the sample appear in the chromatogram. Such behavior is indicative of inlet-induced decomposition.

Iron filings present in commercial glass bead supports also enhance the danger of thermal decomposition during the gas chromatography of diphosphine oxides. These iron filings must be removed prior to the preparation of glass bead columns.

Module temperatures

The research of Bailey and co-workers (5) on the stability of tertiary alkyl phosphine oxides suggests that the diphosphine oxides can be expected to be resistant to thermal decomposition up to the maximum operating temperature (350°C) of silicone columns. Provided a glass system is used, this expectation is borne out.

Flash vaporization inlet temperatures of from 220°C to

400°C have been employed. A temperature of 400°C is unnecessary and does result in a small amount of decomposition. A temperature of 220°C is sufficient for MNDPO, MEBDPO, MHDPO and MEHDPO but results in a broad peak for EHDPO and no peaks for PHDPO and BHDPO. An inlet temperature of 290 ± 10°C has been found to result in sharp traces for all seven diphosphine oxides with no thermal decomposition.

Choice of column temperatures is somewhat more limited. With a four-foot column of five per cent SE-30 on DMCS-treated Chromosorb G and a carrier gas flow rate of 150 ml./min., optimum column temperatures (those yielding a symmetrical peak in approximately five minutes) for MHDPO, EHDPO, PHDPO and BHDPO are 255, 270, 275 and 280°C. Although obtained under somewhat different conditions, Figure 4 demonstrates the capability of isothermal column operation at 280°C. A column temperature of 290 ± 10°C has been found most useful for isothermal separations regardless of small variations in column dimensions. The value of programmed temperature column operation is demonstrated with MNDPO (Figure 3).

Inlet-line, detector-line and detector temperatures are set in accordance with the inlet and column temperatures. Detector-line temperatures of 420°C have been employed without complication.

General comments

The conditions given for Figures 1-4 are typical of those

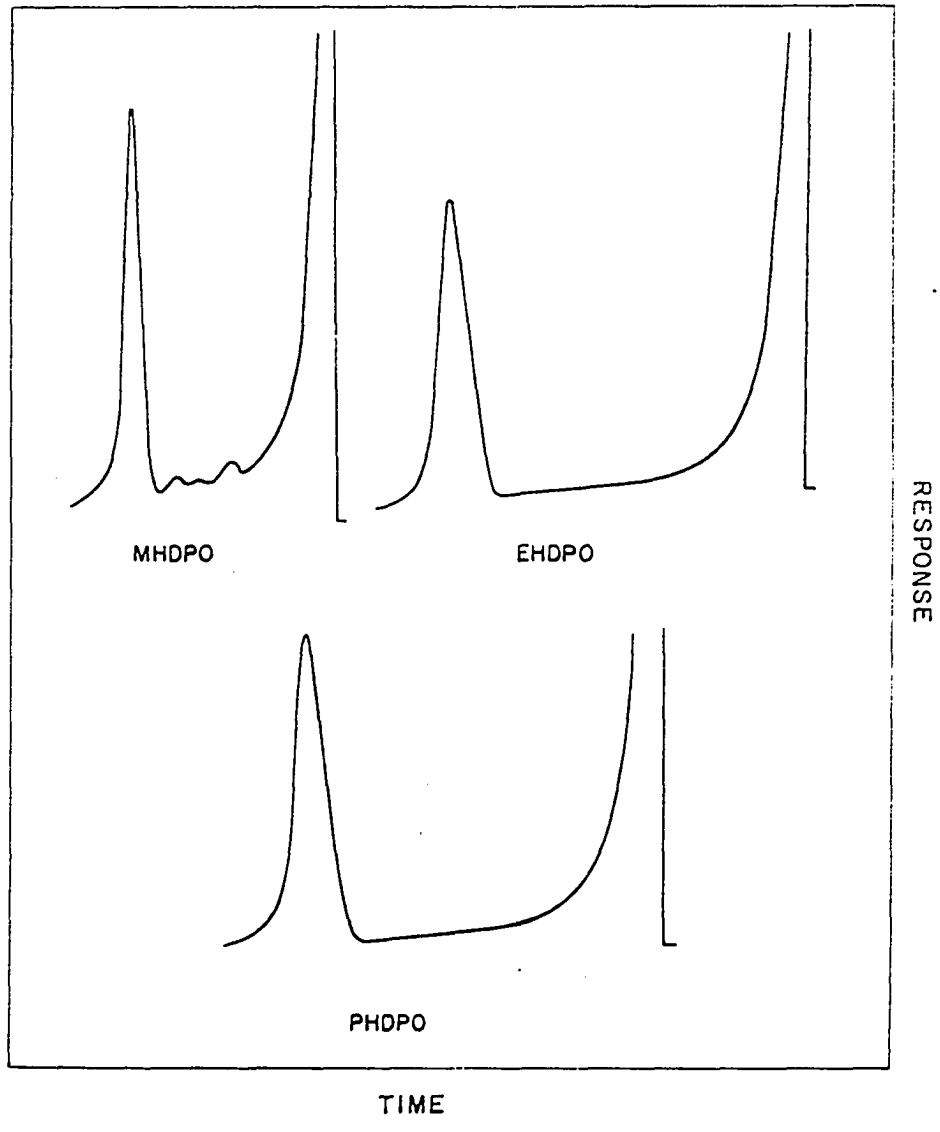


Figure 1. Isothermal gas chromatograms of MHDPO, EHDPO and PHDPO in 1,2-dichlorobenzene

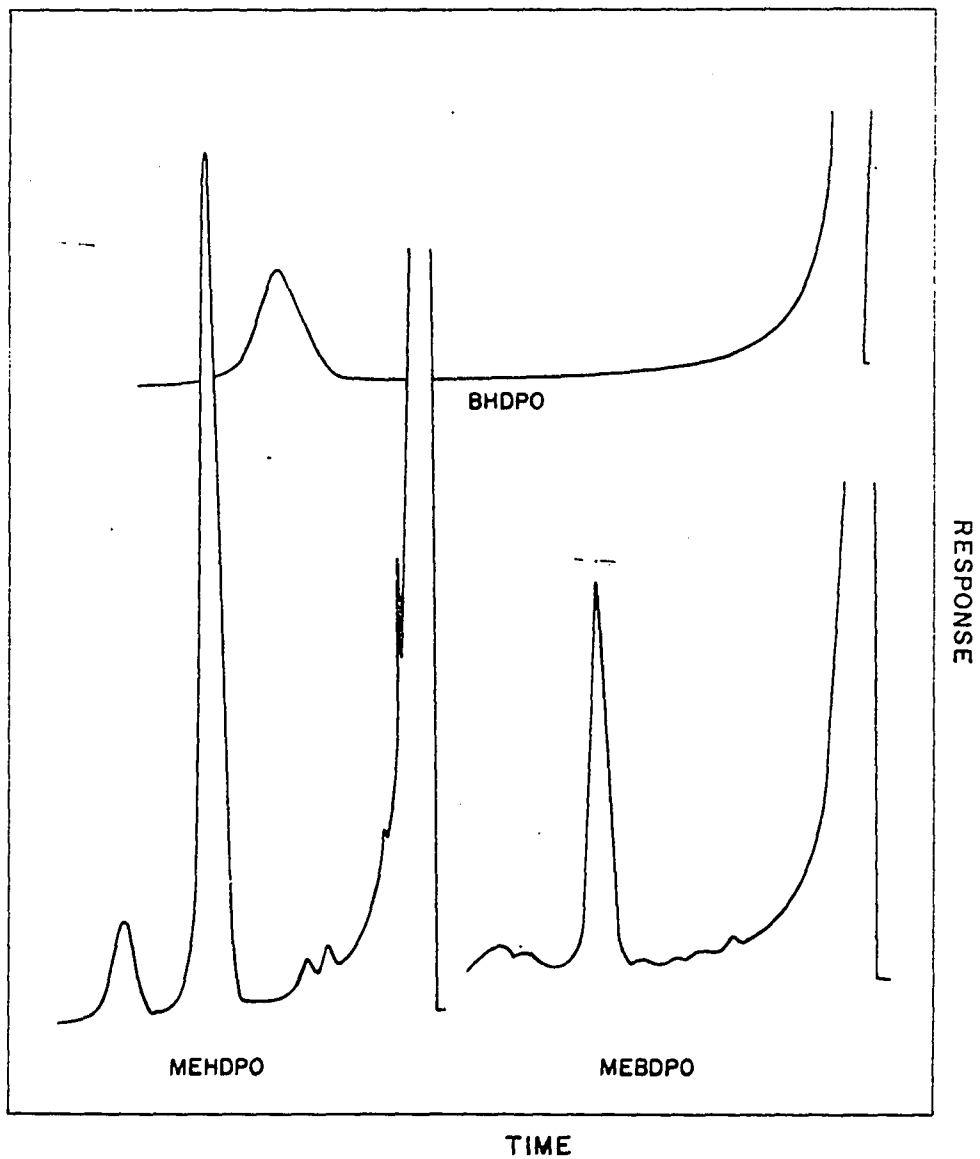


Figure 2. Isothermal gas chromatograms of BHDPO, MEHDPO and MEBDPO in 1,2-dichlorobenzene

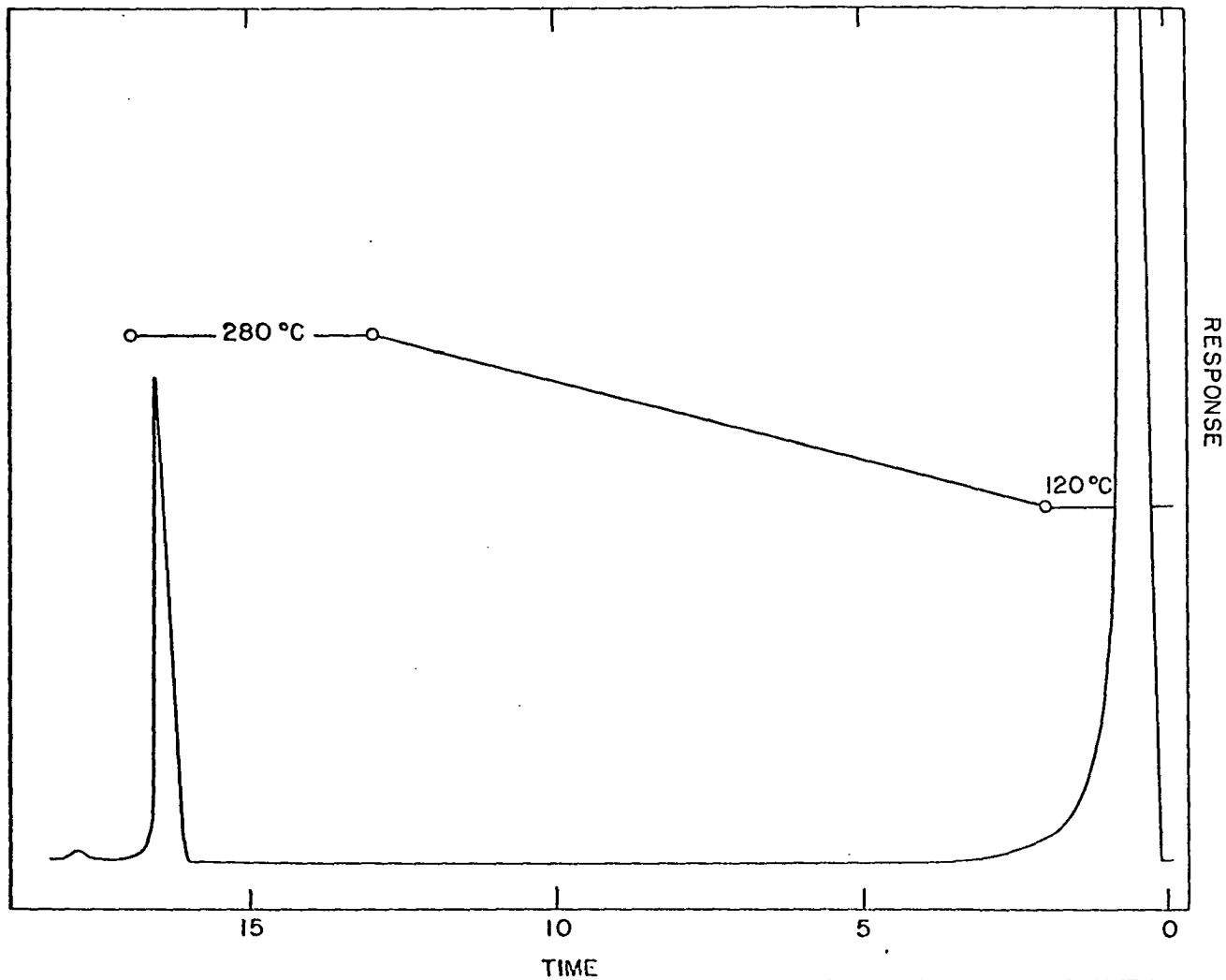


Figure 3. Programmed column temperature gas chromatogram of MNDPO in 1,2-dichloroethane

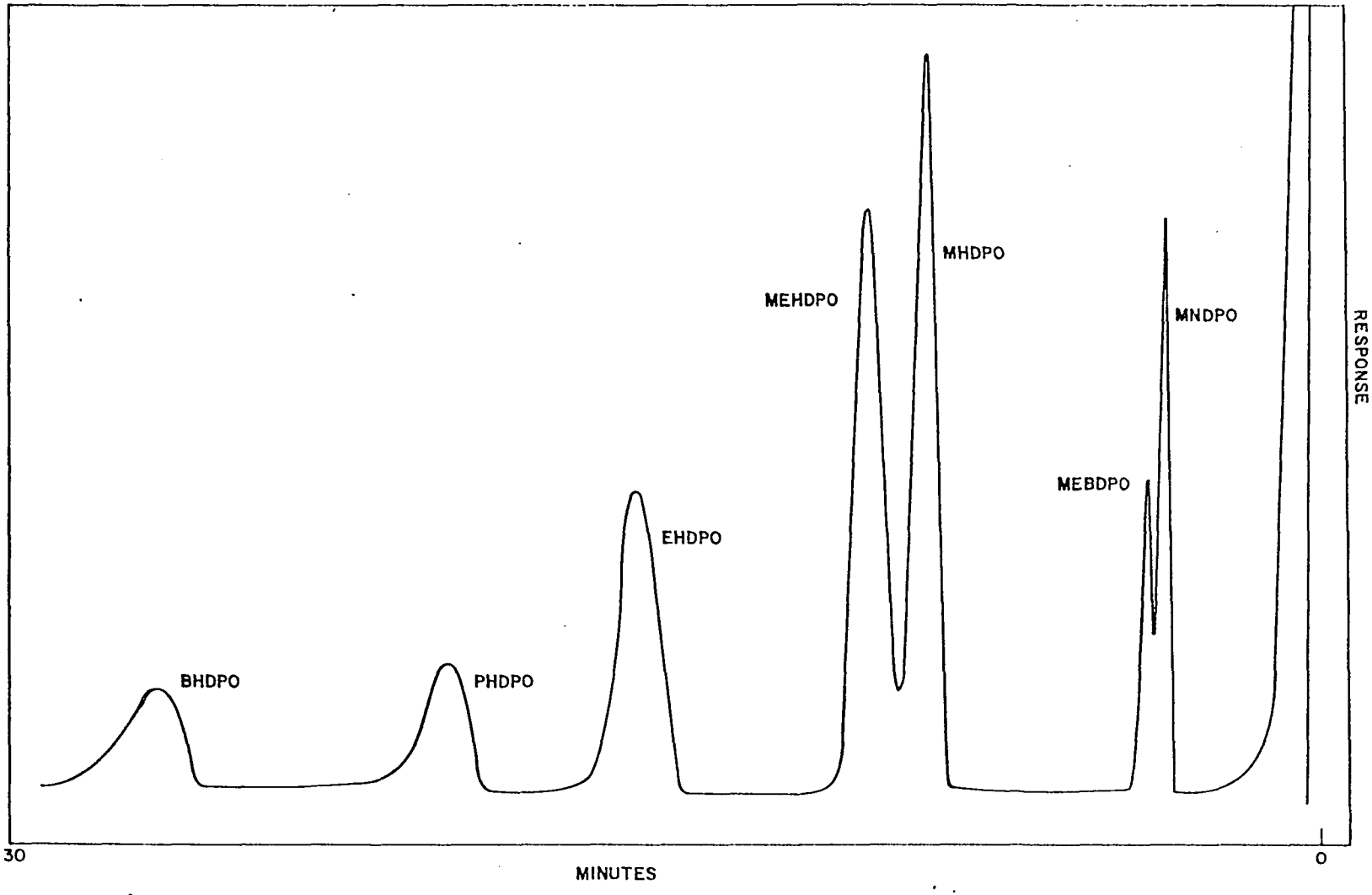


Figure 4. Isothermal gas chromatographic separation of the diphosphine oxides and 1,2-dichloroethane

employed. Although the majority of the work reported was carried out using four-foot, 0.25-inch o.d. columns, several other column lengths and diameters have been employed. Eight-foot, 0.25-inch o.d. columns were found superior to the shorter columns for the resolution of the impurities in MHDPO. Smaller diameter columns (0.125-inch o.d.) result in less sample loss to column adsorption. Very short columns have the advantage that lower temperatures may be used. The quantitative analysis of EHDPO and MNDPO (Table 8) was carried out using a 1.5-foot, 0.125 inch o.d. column.

Because high temperatures are required, success in gas chromatographing the diphosphine oxides is quite sensitive to rather minor procedural changes. On-column injection has been found completely inferior to flash vaporization injection. The importance of the choice of the solid support has already been pointed out. Column conditioning procedures can also have an effect. A silicone column conditioned at 340°C for 40 hours was found inapplicable to the analysis of EHDPO, PHDPO and BHDPO whereas one conditioned at 320°C for 36 hours was perfectly satisfactory for all of the diphosphine oxides.

As is reported for other organophosphorus compounds (11, 23), programmed temperature techniques can be beneficially applied to diphosphine oxide separations. A program allowing isothermal column operation at 270°C for approximately twelve minutes with a subsequent increase to 300°C over a period of

three minutes allows almost baseline resolution of the seven diphosphine oxides with the same column as used to obtain the chromatogram of Figure 4.

Both thermal conductivity and hydrogen flame ionization detection have been employed in these studies. The obvious advantage of flame detection is the ability to use much smaller samples with the resulting improvement in the shapes of peaks and retention data reproducibility (96). Both detectors are well suited to the analysis of the diphosphine oxides.

The mere presence of a peak on injection of a sample into a chromatograph is not evidence that the sample is chromatographable. The peak could as well correspond to a degradation product of the original sample or to an impurity. To be certain that the peaks assigned to the diphosphine oxides do so correspond, the thermal conductivity detector was employed and the column effluent corresponding to the assigned peaks collected. The collected material was submitted for infrared analysis and the spectra compared with standard spectra of unchromatographed diphosphine oxide. Figure 5 shows the agreement between standard and sample spectra for BHDPO. Comparable band position agreement was found for all of the diphosphine oxides. It can be confidently concluded that the peaks assigned to the diphosphine oxides do so correspond. The absence of new bands in the sample spectra supports the contention that little if any decomposition attends the gas

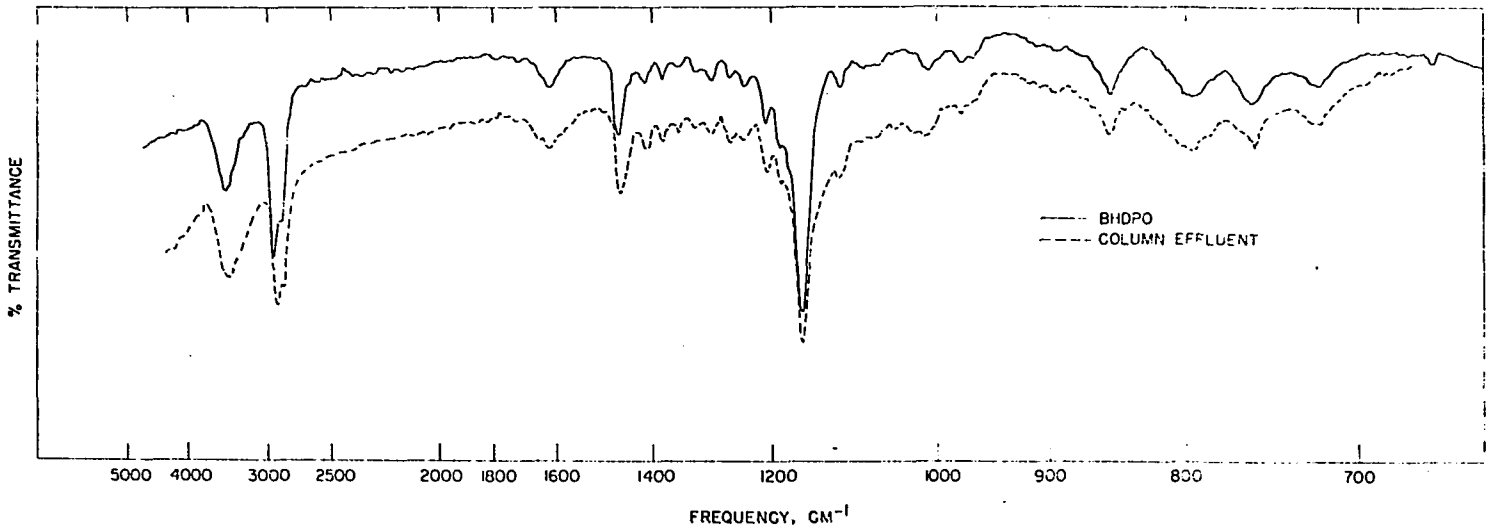


Figure 5. Comparison of the infrared spectra of chromatographed (column effluent) and unchromatographed BHDPO

chromatography of these organophosphorus compounds.

Establishment of peak correspondence allows a meaningful consideration of the retention data. The extent of column adsorption of the diphosphine oxides, the extent of the thermal decomposition of these compounds under chromatographic conditions, and the applicability of gas chromatography to the analysis of diphosphine oxides are considered in later sections of this thesis. Several comments on the retention behavior of the diphosphine oxides can be made here.

Adjusted* retention times of six diphosphine oxides are presented in Table 5. An examination of these data reveals the order of retention of the diphosphine oxides to be BHDPO > PHDPO > EHDPO > MHDPO $\approx$ MEHDPO > MEBDPO. MNDPO was unavailable at the time of these studies but subsequent work indicates that this compound is retained slightly less than is MEBDPO (see Figure 4). The same order of retention of the diphosphine oxides can be expected for any column containing a non-selective (silicone or hydrocarbon) liquid phase.

The adjusted retention times in Table 5 are useful as a measure of the time required for the analysis of the various diphosphine oxides. Because adjusted retention times are greatly dependent on chromatographic conditions, the analysis times derived from the adjusted retention times of Table 5

*Adjusted retention parameters are those measured from the peak of a non-retained compound (generally, air) rather than from the point of injection.

are valid only when the diphosphine oxides are analyzed using the same chromatographic conditions as were employed to obtain the adjusted retention times.

Table 5. Retention data for the diphosphine oxides

Sample	Adjusted retention time[a] (min.)	Retention index[b]
MHDPO	3.6	4970
EHDPO	6.1	5540
PHDPO	7.7	5870
BHDPO	10.1	6230
MNDPO	--	3600
MEBDPO	1.5	3630
MEHDPO	3.9	5070

[a]From airpeak for a 4-ft., 0.25-in. o.d. column of 5% SE-30 on DMCS-treated Chromosorb G operated at 290°C with a flow rate of carrier gas of 150 ml./min.

[b]Above column with column temperature program of 240-340°C in 15 minutes.

Retention indices (35,64) for the diphosphine oxides are also presented in Table 5. Because retention indices are less sensitive to chromatographic conditions than are adjusted retention times, the presented values of the retention indices may be employed with greater confidence than the values of the adjusted retention times for the gas chromatographic identification of the diphosphine oxides.

Because of the unavailability of n-alkanes emerging in the vicinity of the diphosphine oxides under the isothermal operating conditions suitable for this study, the programmed column temperature method of Habgood and Harris (45) was used

for the computation of the retention indices. Using a four-foot SE-30 column with a linear fifteen-minute temperature program covering the range 240-340°C allowed the alkanes n-octadecane and eicosane to be resolved from the solvent (1,2-dichlorobenzene) and displayed the diphosphine oxides prior to the end of the program. These retention indices are necessarily less accurate than those that would be obtained with isothermal column operation.

The availability of the adjusted retention parameters for the diphosphine oxides allows a further test of two concepts important to the identification of compounds from gas chromatographic data (51,63). One of these is that a linear relationship exists between the logarithm of the adjusted retention parameters and the boiling points of compounds of similar structure on columns containing non-selective liquid phases. This relationship, in terms of adjusted retention distances, is demonstrated in Figure 6 for the diphosphine oxides.

An examination of Figure 6 shows that there is a definite relationship between the boiling points and the adjusted retention distances of the majority of the diphosphine oxides studied. The point for tri-n-octylphosphine oxide (TOPO) is included as a measure of the deviation from the predicted retention behavior to be expected from a given change in structure of the chromatographed compound. The greater than expected (on the basis of boiling points) retention of MEHDPO

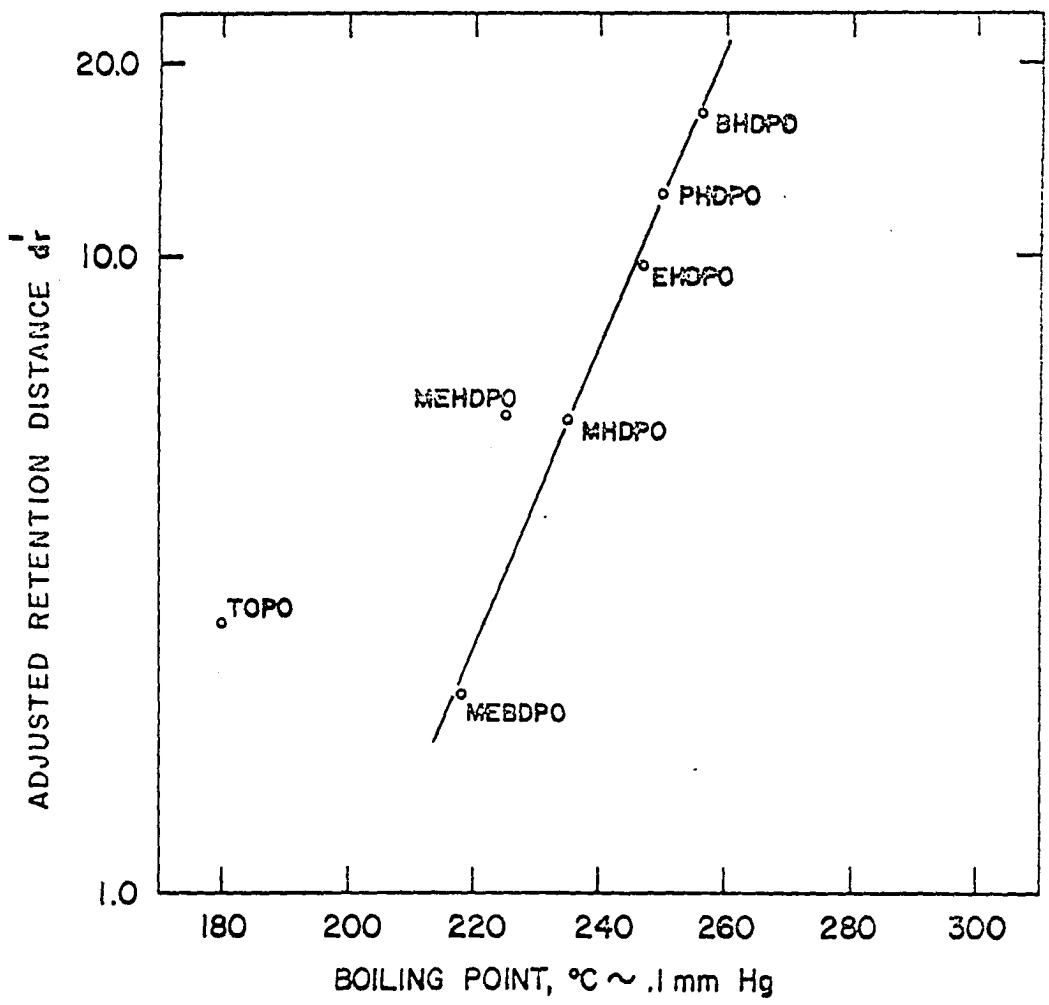


Figure 6. Adjusted retention distances of the diphosphine oxides and TOPO as a function of their boiling points

might be associated with the slightly greater hydrocarbon content of this diphosphine oxide as compared to the diphosphine oxides with six-carbon alkyl chains. The possibility that the relative hydrocarbon content of diphosphine oxides influences the retention behavior of these organophosphorus compounds is supported by the large retention seen for TOPO (having three eight-carbon chains per P-O group).

The second concept that can be tested with the retention data for the diphosphine oxides is that postulating that the structural groups of a compound contribute additively to the logarithm of the adjusted retention distance of the compound and contribute to an extent independent of the compound of which the group is a part. This concept has been best established for homologous series. In this case, the "structural group" is the methylene group.

The diphosphine oxides MHDPO, EHDPO, PHDPO, and BHDPO may be visualized as being formed by the sequential addition of a methylene group to the methylene bridge separating the phosphorus atoms in these compounds. As such, the four diphosphine oxides make up a homologous series. A plot of $\log_{10}$ [adjusted retention distance] versus the number of carbons in the methylene bridges would be expected to yield a straight line as is observed for other homologous series. This relationship is demonstrated in Figure 7 for the diphosphine oxides. A low value for the retention of the lowest member

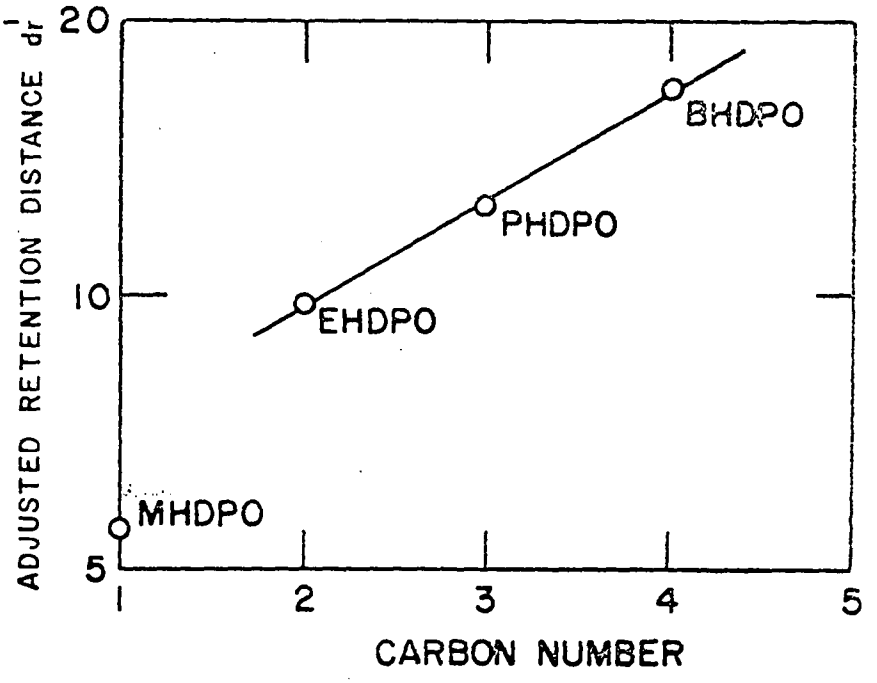


Figure 7. Adjusted retention distance as a function of the number of carbon atoms in the methylene bridge for MHDPO, EHDPO, PHDPO and BHDPO

of a series is commonly observed (63).

The gas chromatography of the uranyl nitrate-diphosphine oxide complexes was briefly considered. The use of high inlet temperatures (450°C) resulted in small peaks of poorly reproducible areas emerging at the positions characteristic of the diphosphine oxides. This suggests that a small amount of ligand is stripped from the metal-ligand complex at high inlet temperatures. At lower (270°C) inlet temperatures, a small peak of reproducible area appeared at the position in the chromatogram characteristic of the ligand. The size of the peak suggested that only the uncomplexed ligand present in the original sample was chromatographed.

Loss of Sample to the Column

Liquid phase and solid support adsorption are common occurrences in gas chromatography (72,89,96). The problem is especially severe when samples of low volatility are chromatographed. Adsorption loss is further complicated for samples of significant polarity.

Results of the loss of sample to the column can include poorly reproducible retention data. Scholz and Brandt (96) claim that for severe cases of support adsorption alone, the reproducibility of retention data can be as poor as 23%. Equally important is the fact that the area of the peaks can be dependent on column history in addition to the size of the sample. This results from the fact that adsorption is a

function of the number of adsorption "sites" and this number can decrease with an increasing number of injections because of irreversible sample adsorption. Allowing the column to be heated and purged with carrier gas for the period of a day or less can remove a significant number of adsorbed molecules with the resulting regeneration of adsorption sites. The net result of this behavior is difficulty in obtaining peaks of reproducible areas.

Dependence of peak area on injection-number

The dependence of the area of a peak on the number of injections of the sample would seem to offer a simple way to obtain a measure of the amount of the sample lost to the column. Injection of a given size sample is continued until no change in the area of the peak is observed with subsequent injections. Knowledge of the size of the sample and constant peak area allows the computation of the units of area per given weight of sample. Provided that the detector responds linearly to the size of the sample, the difference between the area of the peak obtained with the first injection and the last injection yields the weight of sample lost on the first injection. This procedure can be repeated to determine the amount of sample lost on each succeeding injection showing a loss to the column.

Several factors limit the value of this procedure. For one, detector linearity over the range of the sub-microgram

amounts of sample that might be lost to the fractional milligram samples that might be injected is only a fair assumption. More important, it must be assumed that an exactly equivalent amount of sample is injected each time. This is rarely achieved in practice. Finally, a column used for such a study with one solute cannot confidently be used for another because adsorption sites would be neutralized by the original solute.

Regardless of its limitations, the technique offers a simple way to assess the seriousness of sample-loss and to insure that loss is at a tolerable level. Using a simple four-foot, 0.25-inch o.d., 5% SE-30 on DMCS-treated Chromosorb G column at 285°C and sample sizes of 224 and 450 µg. for MHDPO and BHDPO respectively showed that the area of the peaks was independent of injection-number after only two injections of MHDPO but persisted to four injections for BHDPO. Thirty per cent of the original sample was lost on the first injection of BHDPO while only three percent was lost for MHDPO. Although the exact values of the percentages lost are suspect for the reasons described, the values can be used as a measure of the relative seriousness of sample-loss for the various diphosphine oxides. Loss would be expected to be somewhat less than MHDPO for MNDPO and MEBDPO while EHDPO, PHDPO, and MEHDPO would be expected to exhibit behavior intermediate to MHDPO and BHDPO.

Using the same type of column as described above, a

solution containing 100 µg. each of MHDPO, EHDPO, PHDPO and BHDPO was successively injected to determine the number of injections necessary to yield peaks having a constant area. It was found that four injections of this solution were sufficient to cancel the danger of noticeable sample-loss for the period of one day. With subsequent use, the same column exhibited no significant adsorption of the sample after only three injections of any diphosphine oxide.

The number of injections required to saturate the adsorption sites can never be predicted as it is a function of the particular column, column history, and the sample. It has been noted, however, that this number seldom exceeds four for four-foot silicone/DMCS-treated Chromosorb G columns at 290°C regardless of the diphosphine oxide chromatographed. The danger of sample-loss must be kept in mind anytime quantitative analysis is attempted.

Dependence of retention on sample size

Scholz and Brandt (96) noted a sample size dependence of retention data for polar samples chromatographed on columns expected to exhibit support adsorption. These workers reasoned that if this behavior was related to adsorption, it should be representable by the Freundlich isotherm $y = kP^{1/n}$ where "y" is the weight of adsorbate per unit mass of adsorbent, "P" is the equilibrium pressure, and "k" and "n" are empirical constants dependent upon the nature of the solid and gas. Assum-

ing that "y" is proportional to specific retention volume (the more the adsorption the greater the retention) and "P" is proportional to sample size the authors obtained

$$\text{specific retention volume} = k(\text{sample size})^{1/n}.$$

Plotting $\log_{10}$[specific retention volume] versus $\log_{10}$[sample size] for methanol and n-propanol yielded straight lines for each, the methanol data yielding a much larger slope than the n-propanol data. The authors concluded that adsorption was probably playing a part in the retention behavior of the alcohols and that, on the basis of the slopes, methanol was adsorbed to a greater degree than was n-propanol.

A similar study was carried out with the diphosphine oxides. Figure 8 shows plots of $\log_{10}$[adjusted retention distance] versus $\log_{10}$ [microliters of sample] for the diphosphine oxides. The linearity is seen to be good and the slopes (Table 6) vary as might be expected. From these data it can be postulated that the order of seriousness of adsorption is BHDPO > PHDPO > EHDPO > MHDPO > MEBDPO $\approx$ MEHDPO. MNDPO was unavailable at the time of this study. For purposes of comparison with more commonly chromatographed species, tribenzylamine and 2,9-dimethylphenanthroline yielded relative slopes of 0.86 and 0.51 respectively under identical chromatographic conditions.

The greater relative slope for MHDPO than for MEHDPO rules out the possibility of the greater retention of MEHDPO

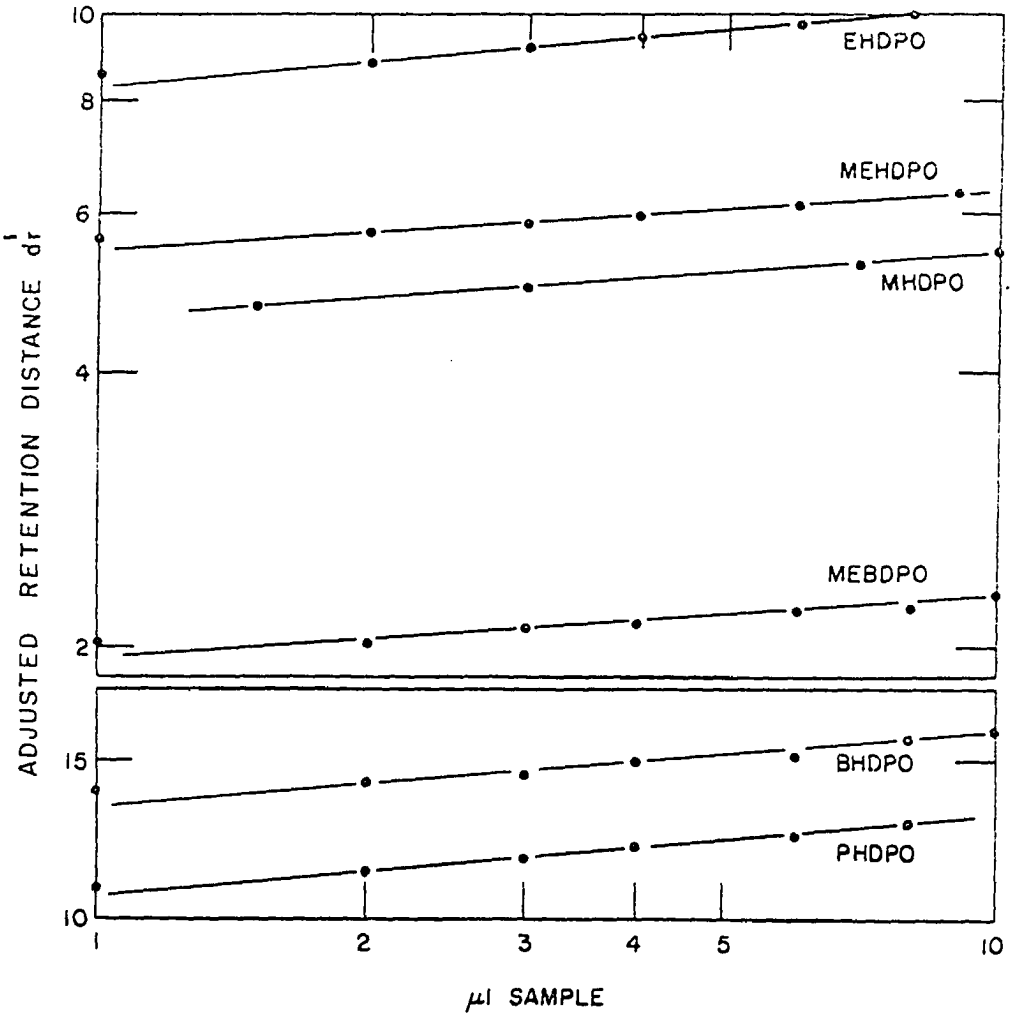


Figure 8. Variation in the adjusted retention distance with increasing sample size for EHDPO, MEHDPO, MHDPO, MEBDPO, BHDPO and PHDPO

than MHDPO being a result of adsorption. This supports the contention that the retention behavior of the diphosphine oxides is significantly influenced by the size of the alkyl side chains.

Table 6. Relative extent of the loss of sample to the column

Compound	Relative slope[a]
MHDPO	0.71
EHDPO	0.82
PHDPO	0.90
BHDPO	1.00
MEBDPO	0.62
MEHDPO	0.62

[a]Slopes of the plots of Figure 8.

It is also interesting to note that the relative slopes of Table 6 increase very regularly from MEBDPO and MEHDPO to BHDPO. The study of the dependence of the areas of the peaks for the diphosphine oxides on the number of injections suggests that BHDPO is much more greatly adsorbed than any other diphosphine oxide. Experience in chromatographing the diphosphine oxides suggests, in fact, that BHDPO is peculiar in the very great amount of sample lost to the column (much greater than PHDPO).

Stability Under Chromatographic Conditions

Several approaches were used in the investigation of inlet- and column-induced thermal decomposition of the diphosphine oxides. Reasoning that any decomposition induced

by the inlet under normal chromatographic conditions would be increased by increased inlet temperatures, the influence of low, normal, and high inlet temperatures on the appearance of chromatograms was chosen as the means of investigating the seriousness of inlet-induced decomposition. Similarly, the influence of column temperature on the appearance of chromatograms was used to investigate column-induced decomposition.

Inlet-induced decomposition

High column temperature Although the reproducibility of the positions and sizes of the minor peaks in the chromatograms of the diphosphine oxides strongly suggest that the peaks correspond to impurities rather than to decomposition products, the possibility of their corresponding to inlet-induced decomposition products of the diphosphine oxides cannot be ruled out. To test this possibility, the flash vaporization inlet was operated at 270 and 390°C with chromatographic conditions such as to display the peak characteristic of the diphosphine oxide and the minor peaks.

If the minor peaks correspond to decomposition products, these peaks would be expected to increase in size at the expense of the major peak as the temperature of the inlet is increased. Monitoring the ratio of the total area of the minor peaks to the area of the major peak should be a sensitive method of detecting decomposition. The sensitivity of this ratio for MHDPO, MEBDPO, and MEHDPO to an increase of

80°C in the inlet temperature is given in Table 7.

Table 7. Influence of inlet temperature on the ratio of the area of the minor peaks to the area of the major peak in chromatograms of MHDPO, MEHDPO and MEBDPO

Compound	Ratio[a] x 10^3, 290°C[b]	Ratio[a] x 10^3, 370°C[b]
MHDPO	92	105
MEHDPO	153	155
MEBDPO	130	133

[a]Area of the minor peaks to the area of the major peak.

[b]Inlet temperature.

The slight decrease in the ratio for MHDPO seeems too small to be reflecting decomposition. The constancy of the ratios for MEBDPO and MEHDPO indicates that the peaks in these chromatograms are not due to decomposition products. Greater confidence can be placed in the data for MEBDPO and MEHDPO than for MHDPO because the minor peaks are more prominent than for MHDPO.

It should also be pointed out that no new peaks appeared in the chromatograms of MHDPO, MEHDPO, and MEBDPO when the temperature of the inlet was raised from 270 to 390°C. Inlet temperatures of up to 420°C have been employed with some diphosphine oxides without the appearance of new peaks.

Low column temperature Pyrolysis of tertiary alkyl phosphine oxides has been shown to result in the formation of 1-olefins in a manner analogous to the formation of olefins

from the pyrolysis of esters of carboxylic acids (5). Temperatures for fifty per cent decomposition of phosphine oxides without beta-hydrogens such as trimethylphosphine oxide are reported to be in the vicinity of 700°C whereas the availability of beta-hydrogens lowers this temperature to 490°C. As a result, the most likely mode of decomposition of the diphosphine oxides at the inlet temperatures used (<400°C) is the formation of olefins from the alkyl side chains. Monitoring the amount of low-boiling hydrocarbons formed at various inlet temperatures offers an additional means of measuring the extent of inlet-induced decomposition of the solute.

This approach has several advantages over the ratio technique discussed above. Because column temperatures sufficient to allow the gas chromatography of five- and six-carbon hydrocarbons are very low for silicone columns, column bleeding is reduced to near zero and it is possible to operate at maximum detector sensitivities. This allows the detection of sub-microgram amounts of breakdown products and thus a confident measure of the severity of the decomposition. Since the areas of the hydrocarbon peaks can be related to the weights of the hydrocarbons, the technique also allows an exact measure of the extent of decomposition (actually, of that decomposition resulting in the formation of small hydrocarbons).

A four-foot column of five per cent SE-52 on DMCS-treated Chromosorb G packed in 0.25-inch o.d. glass tubing operated at ambient temperature with a carrier gas flow rate of 120 ml./min. was found to yield separate peaks for cis- and trans-pentene-2 (a single peak), hexene-1, and n-heptane. The area per microgram of hydrocarbon was obtained for each peak and 10 µl. of 0.10 M solutions of the diphosphine oxides in 1,2-dichlorobenzene were injected at inlet temperatures of 30°C and 400°C. The presence and sizes of the peaks in the hydrocarbon region of the chromatograms obtained were noted for each diphosphine oxide injected.

No hydrocarbon was detected in any of the chromatograms obtained for the diphosphine oxides at inlet temperatures of 30°C. At inlet temperatures of 400°C, injections of the solutes MHDPO, EHDPO, PHDPO, BHDPO, and MEHDPO resulted in the formation of approximately 0.02 µg. of hydrocarbon each while MEBDPO formed 0.04 µg. This corresponds to the formation of a maximum of approximately 0.01 per cent hydrocarbon for MEBDPO and 0.005 per cent for the other diphosphine oxides.

The data indicate that an insignificant amount of sample is lost to inlet-induced decomposition under normal chromatographic conditions. Because the detector sensitivity used in the high column temperature studies was much lower, decomposition of this magnitude would go undetected. This further supports the contention that the minor peaks in the diphos-

phine oxide chromatograms are impurities.

Programmed column temperature In view of the above work, it is extremely unlikely that any inlet-induced decomposition is occurring. The possibility that decomposition products were formed but undetected as a result of emerging under the solvent peak or major peak, though small, exists. To evaluate this possibility, the diphosphine oxides were injected at a normal inlet temperature (300°C) and the temperature of the column was programmed from 120 to 320°C over a period of fifteen minutes. No peaks other than those observed in the isothermal chromatograms were visible.

Column-induced decomposition

Column-induced decomposition is generally recognized by poorly shaped peaks. The symmetrical nature of the peaks for the diphosphine oxides suggest that such decomposition is not occurring.

To further test this possibility, a solution of MHDPO, EHDPO, PHDPO, and BHDPO was chromatographed at 270°C and at 300°C. No additional peaks or changes in the shapes of the peaks (other than the expected broadening) were observed. During the course of these studies, MNDPO was chromatographed at column temperatures of 250°C to 320°C without observing any indication of column-induced decomposition.

It must be recalled that these observations (both the inlet and column studies) apply to glass systems. Use of

metal columns or inlets that are not glass-lined results in extensive decomposition.

Quantitative Analysis

The much greater sensitivity of the hydrogen flame ionization detector as compared to the thermal conductivity detector makes the ionization detector the one of choice for the quantitative analysis of low concentrations of the diphosphine oxides. The injection of one microgram of MHDPO has been found to yield a peak one thousand times as large with the ionization detector as with the conductivity detector. For the analysis of macro levels of the diphosphine oxides, the thermal conductivity detector is as useful as the ionization detector.

Areas and heights of peaks may be used with equal confidence in the analysis of the diphosphine oxides over small ranges of concentration. Figure 9, constructed from data obtained with the ionization detector, demonstrates the relationship between the heights of the peaks for various diphosphine oxides and the weights of the diphosphine oxides subjected to analysis. Over the range of sample size cited in Figure 9, the plots for all of the diphosphine oxides except BHDPO pass through the origin. The BHDPO curve yields a peak height of zero at approximately two micrograms of injected BHDPO.

Table 8 demonstrates the accuracy and precision of an

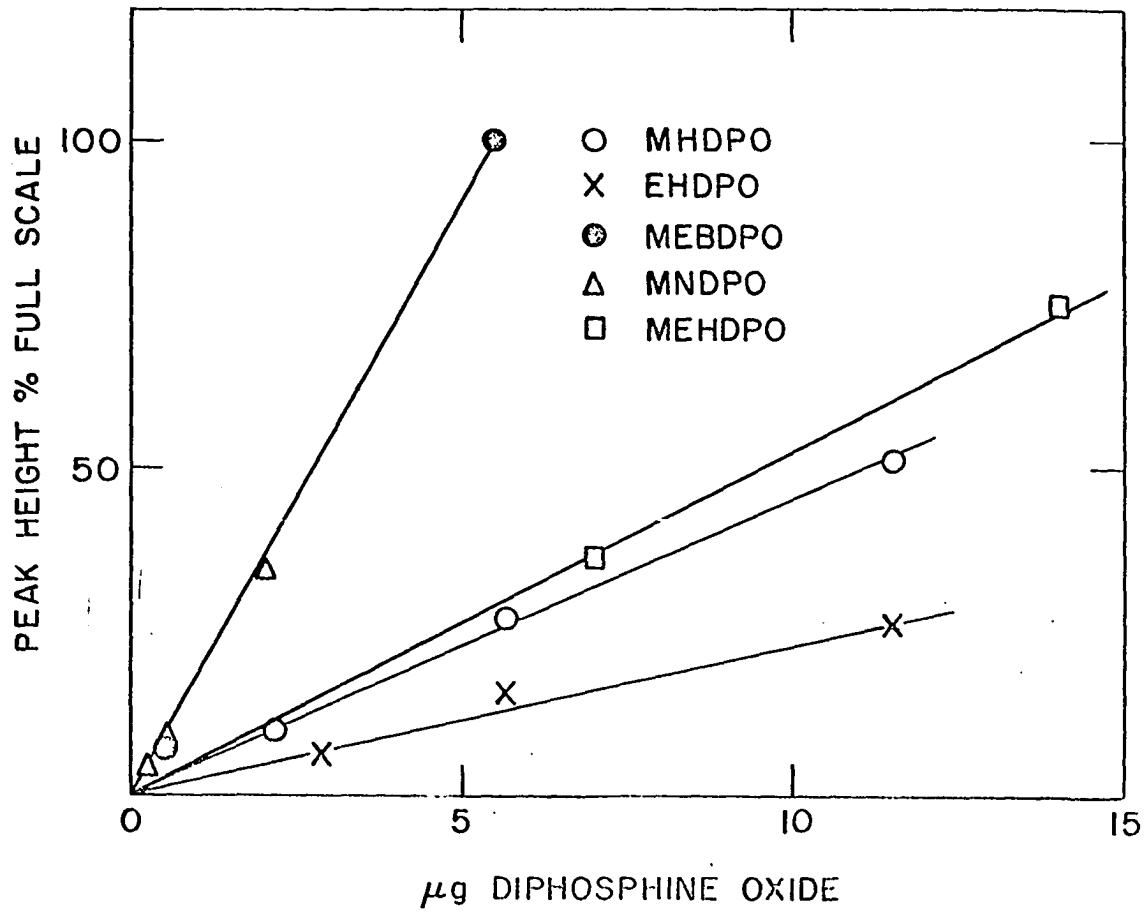


Figure 9. Calibration curves in terms of peak height for the quantitative analysis of the diphosphine oxides MHDPO EHDPO MEBDPO MNDPO and MEHDPO

analysis of EHDPO and an analysis of MNDPO. The analyses were carried out by injecting 1.0 µl. of solution of each diphosphine oxide and converting the areas of the sample peaks to micrograms of diphosphine oxide with the aid of calibration curves. Each point on the calibration curves represented the average area of three injections of each standard while the area of the sample peak was determined from four injections of the sample.

Table 8. Results of the gas chromatographic analysis of EHDPO and MNDPO

Sample	Known (µg)	By analysis (µg) Mean	Range
EHDPO	1.92	1.94	0.19
	0.64	0.54	0.02
MNDPO	2.61	2.60	0.15
	1.37	1.26	0.10

It is useful to determine response factors (the area of the solute peak per given weight of the solute) for the diphosphine oxides. Separate solutions of MHDPO, EHDPO, PHDPO, BHDPO, MEHDPO, and MNDPO in 1,2-dichloroethane were prepared to contain 1.06, 2.02, 0.97, 1.01, 1.37, and 2.02 milligrams of diphosphine oxide per milliliter of solution respectively. Known volumes (1.0 microliter) of each solution were injected at least three times and the areas of the peaks corresponding to the diphosphine oxides were measured. Dividing the average area of the peaks for each diphosphine oxide by the weight of

the diphosphine oxide injected into the chromatograph and multiplying by the detector attenuation yielded the flame ionization detector response factors of Table 9.

Table 9. Response factors for the diphosphine oxides and eicosane

Sample	Response factor[a]	Relative response per microgram of carbon
Eicosane	304	1.00
MHDPO	152	0.64
EHDPO	131	0.55
PHDPO	173	0.72
BHDPO	174	0.72
MNDPO	146	0.62
MEHDPO	157	0.63

[a]Peak area (disc units x 10^{-4}) per microgram of sample.

A comparison of the response factors of the diphosphine oxides with that of a hydrocarbon gives a measure of the influence of the non-hydrocarbon portion of the sample on the flame ionization detector response. Because the response to hydrocarbons is the maximum possible for this type of detector, the comparison also gives a measure of the percentage maximum response for the diphosphine oxides. Response factors per microgram of carbon were computed for the diphosphine oxides and were compared to the corresponding factor for eicosane. The relative response factors are presented in Table 9.

These data show that the detector response to the diphosphine oxides can be expected to be approximately sixty per

cent of that to hydrocarbons. Although no extensive correlation between the structures of the diphosphine oxides and the detector response is possible, it is interesting to note that a significantly higher relative response is obtained for diphosphine oxides containing three- and four-carbon methylene bridges than for those containing shorter bridges.

The response factors of Table 9 may also be used to compute detection limits for the diphosphine oxides. The significance of these limits is highly dependent on the manner in which they are defined. Assuming that a peak large enough to be "detected" is one yielding an integrator trace of ten units (1/10 of one sweep of the integrator pen) at maximum detector sensitivity, it can be shown that the gas chromatographic analysis of the diphosphine oxides is applicable to concentrations of the order of 10^{-9} to 10^{-10} M. Such a detection limit is of little value.

A peak large enough to yield an integrator trace of ten units is much too small, particularly for a peak of any appreciable width, to have much quantitative analytical value. More importantly, operation of a flame ionization detector at its maximum sensitivity is generally very difficult. This is especially true for any analysis requiring high column temperatures.

A readily accessible quantitative detection limit is more useful. Defining the smallest peak large enough for

quantitative analysis to be one yielding an area of two-hundred units (two complete sweeps of the integrator pen) at 1/100 of the maximum detector sensitivity and assuming that ten microliters of the sample-containing solution will be subjected to analysis allows the computation of the more meaningful quantitative detection limits. With the detection limit defined as above, the response factors of Table 9 yield the detection limits of Table 10. Diphosphine oxides present at concentrations lower by a factor of ten than those presented in Table 10 may be quantitatively determined without serious complications. The true detection limits reside at some level between the ideal and the quantitative limits.

Table 10. Quantitative detection limits of the diphosphine oxides

Molarity x 10^6					
MHDPO	EHDPO	PHDPO	BHDPO	MNDPO	MEHDPO
2.9	3.3	2.4	2.3	3.0	2.3

SUMMARY

Conditions are established for the gas chromatography of diphosphine oxides. A four-foot, 0.25-inch o.d. column of five per cent SE-30 impregnated on DMCS-treated Chromosorb G operated at 290°C with a carrier gas flow rate of 120 ml./min. is found to be generally applicable to the gas chromatographic analysis of the diphosphine oxides MNDPO, MEBDPO, MEHDPO, MHDPO, EHDPO, PHDPO, and BHDPO provided that all-glass construction is employed. The use of a metal column and/or metal flash vaporization inlet results in a significant amount of sample decomposition. The use of non-silanized solid supports results in poorly shaped chromatographic peaks for all of the diphosphine oxides.

The peaks assigned to the diphosphine oxides are shown to so correspond by the comparison of the infrared spectra of the unchromatographed diphosphine oxides with the spectra of the column effluent corresponding to the chromatographic peaks of the diphosphine oxides. For columns containing silicone liquid phases (SE-30 or SE-52), the order of retention of the diphosphine oxides is BHDPO > PHDPO > EHDPO > MEHDPO > MHDPO > MEBDPO > MNDPO. The adjusted retention distances of the diphosphine oxides BHDPO, PHDPO, EHDPO, MHDPO, and MEBDPO are related to their respective boiling points. The adjusted retention distances of EHDPO, PHDPO, and BHDPO are also related to the number of methylene groups in their respective methy-

lene bridges.

Inlet- and column-induced decomposition of the diphosphine oxides is studied by examining the influence of the inlet and column temperatures on the appearance of the chromatograms of the diphosphine oxides. No evidence of either inlet- or column-induced decomposition of these compounds is noted for normal chromatographic conditions.

The seriousness of the loss of the diphosphine oxides to the column during the gas chromatography of these samples is examined by studying the dependence of retention data on the size of the sample injected into the chromatograph and by noting the number of injections required to produce peaks having constant areas. These studies indicate that the amount of sample lost to the column is insignificant or can be made insignificant.

The response of the flame ionization detector to the diphosphine oxides is measured and the response factors are computed. The response factors are used to compute quantitative detection limits for the diphosphine oxides and are compared to the response factor for eicosane to obtain a measure of the influence of the phosphoryl groups on the response of the detector to the diphosphine oxides. The quantitative detection limit for the diphosphine oxides is found to be approximately 10^{-6} M. Although no extensive correlation between the response factors for the diphosphine

oxides and the structures of these compounds is possible, a larger relative (to eicosane) response is noted for the diphosphine oxides containing three- and four-carbon methylene bridges than for those containing shorter bridges. The results of the gas chromatographic analysis of MNDPO and EHDPO are presented.

PART II. FRAGMENTATION-GAS CHROMATOGRAPHY OF DIPHOSPHINE OXIDES AND URANYL NITRATE-DIPHOSPHINE OXIDE COMPLEXES

REVIEW OF THE LITERATURE

General Comments

One of the early advocates of combined pyrolysis-gas chromatography as an analytical tool is Janak (53). His enthusiasm appears to have been well based as is evidenced by the acceptance of the technique by workers in many fields. Kirk (62), in discussing the growing importance of the technique in criminalistics states, "It now appears that none of the methods that are used for identification and individualization surpass pyrolysis-gas chromatography in the ability to discriminate closely between similar samples". Kuelemans (59) sums up the value of the technique as a structural analytical tool in his "label" of pyrolysis-gas chromatography - "poor man's mass spectroscopy". Perry (86) states, "The day may not be far away when this technique occupies a position as important as mass and infrared spectroscopy in the identification of any organic (and many organo-metallic) compounds". Although in an earlier phase of development, quantitative analytical applications have also met with considerable success (14,36,54,67,100,105). Applications of the technique have continued to grow.

A literature review of the field covering the period 1960 to 1963 (74) contains more than 200 entries. In this period, 44 papers appeared concerning the pyrolysis-gas chromatography of polymers, 42 concerning hydrocarbons, 21 applying the

method to esters and another ten for organic acids. Eighty-six compounds or compound classes (ranging from quaternary ammonium hydroxides (20,107), through classes like soil humic acids (79) and alkaloids (53) to specific compounds like bicycloheptatriene carboxaldehyde (17)) are presented as having been studied by the pyrolytic method. Bibliographies on the literature of gas chromatography since 1963 (41,92) contain an additional one hundred references to the use of pyrolysis-gas chromatography. In the past six months, micro-organisms have been characterized by the technique (93)and improved methods for the analysis of amino acids, peptides and proteins (75) as well as hydrocarbons (22) and polymers (30,66,66)have been reported.

Although a very simple extension of conventional gas chromatography, the fragmentation method presents many challenging problems and exciting potentialities. By far the most fruitful application of the technique to date is to structural confirmation by way of comparison with standards. True structural analysis is hampered by difficulties in identifying the fragmentation products for any species other than simple hydrocarbons but progress has been made with the application of the retention index concept (32,35,45,64). Quantitative analytical applications have been hampered by the difficulty of obtaining reproducible fragmentation conditions.

Fragmentation Units and Applications

Pyrolyzing the sample in a chamber separate from the chromatograph is the oldest technique employed and has the advantage that fragmentation can be carried out under special, (70), carefully controlled conditions. After pyrolysis, in a sealed glass ampule, the sample is transferred to the carrier gas line by any one of a number of methods (63,103,105). The ampule is then broken and the carrier gas is allowed to flush the pyrolysis products onto the analytical column. The quantitative determination of the hydroxyethyl group of hydroxyethyl starch was carried out using this method (105).

Great emphasis has been placed on making the technique a one-system method, that is, in developing procedures by which the sample can be degraded in the gas stream thus avoiding the extra steps in sampling and sample transfer. One of the more successful techniques has been the use of electrically heated filaments or ribbons on which the sample is deposited (6,13,55,57,86). In those cases of insufficient solubility to allow solution and deposition, the sample is often placed, as the solid, among the coils of the filament or wrapped in a suitable material and placed in the coil. With the sample in place, the filament assembly is placed in the carrier gas line and purged with the carrier gas. The sample is then degraded with a burst of current through the filament, the temperature being controlled by the voltage applied. As they are formed,

the degradation products are swept out of the fragmentation chamber and onto the head of the analytical column where separation occurs.

Filament techniques have found great application to polymer studies (2,7,30,66). Biochemically important species such as purines and pyrimidines (54), phorphyrins (67), amino acids and proteins (75,115) and alkaloids and oils (53) have also been found conveniently handled by filament pyrolyzers.

Closely related to filament pyrolysis is the cup technique of Nelson and Kirk (80,81) used in the study of barbituric acids. In this case, the sample is deposited on a small electrically heated "cup" rather than filament. A similar unit is reported by Perry (87) for the analysis of zinc dialkyl dithiophosphates.

What might be called "in-line reactors" have also received considerable attention as fragmentation units (13,21, 22,32,36,46,57,86). These units are also electrically heated but do not involve filaments. The heating element is generally coiled around or embedded within a cylindrical reactor with a central tubular cavity that is part of the carrier gas flow line. Provisions are made to allow the introduction of solid samples (usually in a quartz boat) into the heated zone (91). Generally, these units can also be used by way of syringe-injection of the sample.

The simplest in-line reactor is the flash vaporization inlet of a normal gas chromatograph. Burke (19) describes

this "direct injection" technique. A unit slightly more complicated has been reported by Dhont (32,33) as highly satisfactory for the structural characterization of aromatic compounds and identification of functional groups in five-carbon aliphatic compounds. Cox has described a microreactor for polymer analysis (21). Kuelemans and co-workers (22,59, 60,61) have described in-line reactors yielding highly reproducible fragmentation patterns for the vapor phase degradation of hydrocarbons. Vassallo (109) has described a modified thermobalance furnace as a fragmentation unit. Smith, Wetzel, and Kosters (100) have reported the use of an in-line reactor in the qualitative and quantitative analysis of benzoates.

More elaborate reactors have been reported. An electrical discharge pyrolyzer (101,102) in which the sample is degraded by a high voltage-low current arc is reported. Martin and Ramstad (71) have described a flash pyrolysis unit in which the sample is pyrolyzed by flashing intense radiant energy from either a carbon arc or xenon flash tube. A paper (98) has recently appeared describing an induction pyrolyzer.

The majority of the cited units may be used for any sample ranging from slightly volatile to non-volatile. With modification, many may be applied to the vapor phase fragmentation of easily volatilized samples. Occasionally, two versions of the same unit are made available; one for vapor phase and the other for solid fragmentation. The electrical discharge pyrolyzer (101,102) is one such case.

Although many problems confront those interested in developing fragmentation-gas chromatography to its potential, the problem of producing a controlled, reproducible fragmentation device for solid samples is outstanding. In discussing the extreme sensitivity of fragmentation patterns to fragmentation conditions, Juvet, Tanner, and Tsao (57) point out that fragmentation temperature and time, sample size, carrier gas flow rate, fragmentation chamber geometry and construction materials can all have influences. Perry (86), in comparing filament pyrolyzers with in-line reactors, points out that the sampling technique used with filament pyrolyzers makes it very difficult to determine the exact amount of sample fragmented, that residual solvent can contribute to the fragmentation pattern, filaments can catalyze decomposition, measurement of filament temperature is difficult and at best yields an approximate temperature and that the lifetime of coiled filaments is often short and attended by a change in operating characteristics. Other workers (57) point out that while in-line reactors would seem to be better fragmentation units, pattern reproducibility is not significantly improved with their use in solid sample degradation.

As a result of the reproducibility problem, Juvet, Tanner, and Tsao (57) have proposed a photolytic degradation mechanism, and reported the application of mercury-sensitized photolysis to a large number of compounds. A high degree of

reproducibility was reported.

Chromatography and Data Treatment

Conditions required for the gas chromatography of the products of fragmentation do not differ from those of conventional gas chromatography. It must be kept in mind, however, that the conditions chosen will dictate the fragments detected and the shapes and retention data of the various peaks. Once chosen, chromatographic conditions must be reproduced if reproducible fragmentation patterns are desired.

Whereas the ability to select the fragmentation products detected can be a great asset, the detection of only a small number of products can be a serious complication in any case where the important types of degradation products are not known prior to the analysis. The availability of programmed temperature techniques capable of operating from sub-ambient to high temperatures lessens the complication. The pyrolyzate may be subjected to such a programmed temperature separation using a screening column, the fragmentation region of interest chosen, and conditions developed for the high resolution of the important breakdown products. These conditions would then be used for subsequent analyses.

Methods used for quantitative analysis with fragmentation-gas chromatography are, for the most part, identical to those used in conventional gas chromatography. Generally, the

amount of sample present is related directly to the area or height of a given peak in the pattern or to the ratio of peak sizes when internal standards are employed. Smith, Wetzel and Kosters (100) determined the extent of decomposition of benzoates by simply monitoring the ratio of peak sizes of the decomposition products to the undecomposed benzoate. Bhatnagar and Dhont (14) used a conventional internal standard technique in the analysis of benzene clathrate. Ettre (36) has studied the quantitative analysis of polymers using peak ratios. The ratio of ethanol to acetonitrile served as a measure of the extent of haematoporphyrin contamination in a given grade of protoporphyrin (67). Examples of quantitative analysis based on the sizes of single peaks are also available (54,105).

Characterizing fragmentation patterns for qualitative analysis presents a different problem. Whereas qualitative reproducibility on a given column under given conditions far surpasses quantitative reproducibility of the patterns, comparison between columns often results in very poor reproducibility. This is a result of the fact that the position of the peak is very dependent on chromatographic conditions and is the important parameter for qualitative analysis.

This difficulty is associated with the long-standing problem of the preparation of reproducible columns. As such, the most fruitful approaches to characterizing breakdown

patterns have been those applying retention parameters of low sensitivity to chromatographic conditions. Of these parameters (35,37), the "retention index" (33,35,45,64) seems most useful.

Dhont (33) presents fragmentation patterns in a manner analogous to the presentation of mass spectra but with retention index in place of m/e. A relationship between boiling point and retention index has also been used to identify certain fragments (33). Other workers (57) take advantage of a relation between retention indices of product and parent peaks to characterize fragmentation patterns.

Franc and Blaha (40) removed the requirement for the reproducibility of the position of the peaks by limiting the number of fragments formed. These workers degraded samples to H_2, CO, CH_4, and CO_2 and characterized the breakdown patterns in terms of the relative amounts of each formed. It is shown possible to identify aromatic ring substituents in this manner.

Organophosphorus Compounds

Relatively little has been reported on the application of fragmentation-gas chromatography to the analysis of organophosphorus compounds. Work on phosphates and thiophosphates (65,87) has resulted in a convenient way to characterize the alcohol used in the preparation of these esters. A thorough

investigation of the pyrolysis of tertiary phosphine oxides (5) was aided by a preliminary study using in-line pyrolysis. One additional reference (34) to organophosphorus fragmentation-gas chromatography is cited in a review (23).

Studies of the behavior of many organophosphorus compounds on pyrolysis have been reported. Baumgarten and Setterquist (9) investigated the mild pyrolysis of alkyl phosphates as a sequel to other workers studies of the pyrolysis of esters of carboxylic acids and reported that the pyrolysis of phosphates yields olefins through a mechanism analogous to that involved in the pyrolysis of esters of organic acids. Quantitative recovery of olefin was reported for dialkyl and trialkyl methyl phosphates. Studies of the radiolysis (114) and pyrolysis (48) of tri-n-butyl phosphate yielded similar results. The general value of the pyrolysis of organophosphorus compounds in synthetic organic chemistry is exemplified by the large number of publications on the topic (8,10,25,26,27,28,42,108,110).

The work of Bailey, Muir, and Marktscheffel (5) on the thermal stability of tertiary phosphine oxides is especially pertinent to this thesis work. These workers found that the monophosphine oxides yielded 1-olefins as a result of the cleavage of the C-P bond at pyrolysis temperatures ranging from 350-600°C. Finding extremely high thermal stability for trimethyl and triphenyl phosphine oxide suggested the impor-

tance of beta-hydrogen in the pyrolysis mechanism. It was reported that the data were well interpreted using a cyclic mechanism analogous to that of ester pyrolysis. Similar results have been reported for alkyl phosphoramidates (8) and alkyl phosphinates (10).

The secondary phosphine oxide remaining after the removal of an alkyl group was found to either air-oxidize to the corresponding phosphinic acid or disproportionate to a phosphine and phosphinic acid. The secondary phosphine oxides resulting from the pyrolysis of compounds containing alkyl groups of four or more carbons were found sufficiently stable to isolate.

Metal Complexes

The only report of the fragmentation-gas chromatography of metal complexes is that of Burke (19). In studying direct injection as a pyrolysis tool, copper and chromium acetylacetonates were found to yield reproducible amounts of unbroken ligand which could be used to determine both the number and type of ligands bound to metal.

Although not involving gas chromatography, the work of Wendlandt, Iftikhar, and Stembridge (112) is worthy of note. These workers used pyrolysis-mass spectroscopy and demonstrated the ability of the complexed metal to influence the relative amounts of breakdown products formed on the pyrolysis of metal-cupferrates. Studies (31) of thermogravimetric analysis have also shown complexation to influence breakdown modes.

EQUIPMENT, MATERIALS AND PROCEDURES

Equipment

A diagram of the Beckman GC-4 electrical discharge fragmentation-gas chromatograph assembly (102) is given in Figure 10. The components are listed with the figure. Figure 11 gives an exploded view of the sample tube assembly and diagrams the sample loading procedure.

Control of flow rates of the carrier gas is maintained with flow controllers for the column lines and a pressure controller for the sample tube line. Discharge voltage is controlled with a variac (3500-volt maximum). The voltage control is calibrated in percentage of the maximum voltage to the nearest 2.5%. Discharge current is read from a meter in milliamperes. Currents from 0.4 to 90.0 milliamperes may be used. The discharge time may be set at five to sixty seconds.

The switching valve is used to direct the appropriate carrier lines through the sample loop (a coiled stainless steel tube of ten cubic centimeter capacity). In the "purge" position, carrier gas passes through the sample tube, sample loop, and, finally, is vented to the atmosphere. In the "inject" position, carrier gas is passed through the sample loop and into the analytical column.

The valve compartment allows heating of the fragmentation portion of the assembly. Of necessity, the switching valve, sample loop, and sample tube are operated at the same,

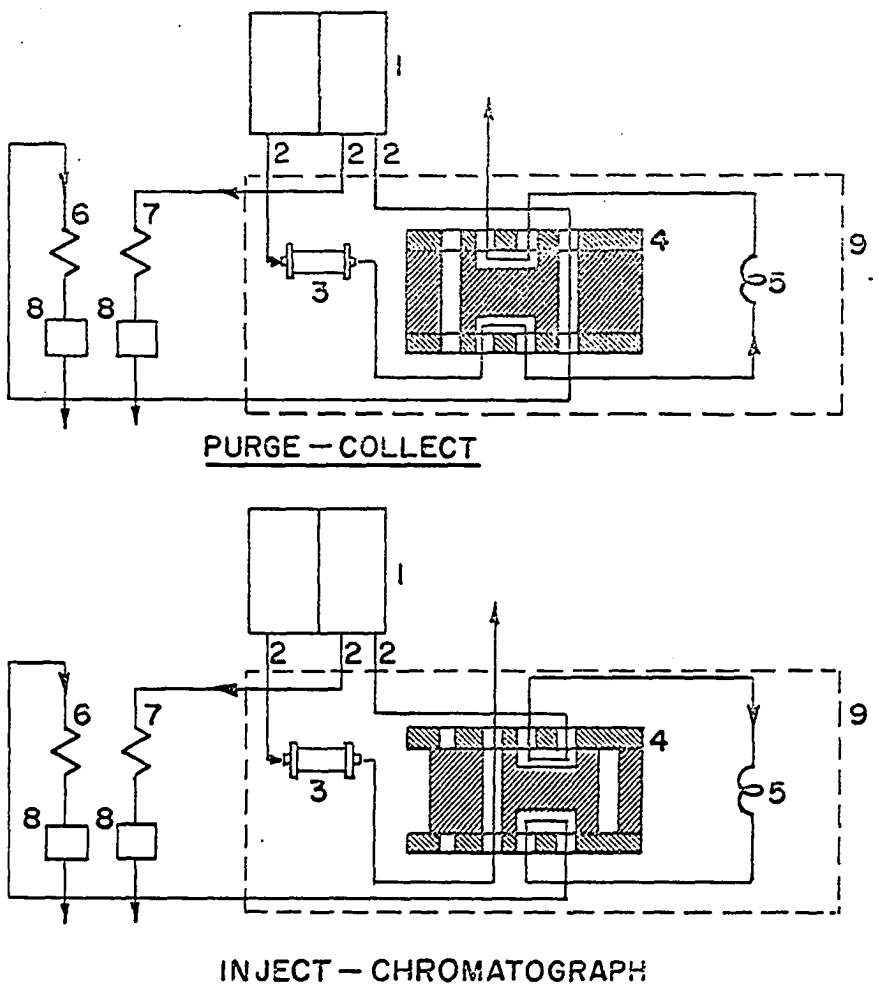


Figure 10. Operating modes of the Beckman fragmentation-gas chromatography assembly; 1. Flow controls 2. Carrier gas lines 3. Sample tube assembly 4. Switching valve 5. Sample loop 6. Analytical column 7. Reference column 8. Detectors 9. Valve compartment

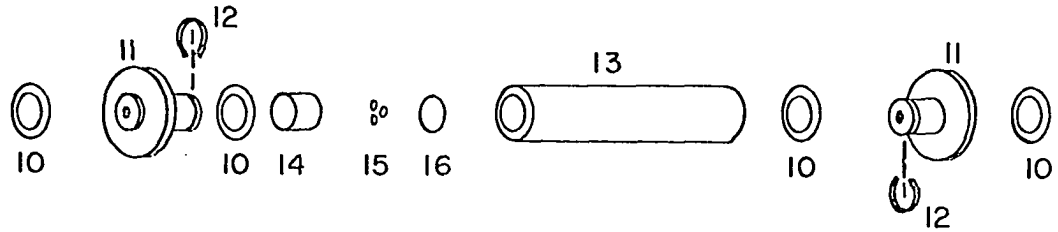


Figure 11. Sample tube assembly; 10. Lead gaskets 11. Electrodes 12. Retainer springs 13. Sample tube 14. Carbon wool 15. Solid sample 16. Silica wool

constant temperature.

Materials

The diphosphine oxides and corresponding uranyl nitrate complexes used in these investigations are those described in "Part I" of this thesis. The standard 3,3-dimethylbutene-1 was obtained from Columbia Organic Chemicals. The standards 3-methylpentene-2 (mixture of cis and trans), 2-methylpentane, 2-methylpentene-2, trans-3-methylpentene-2, cis-3-methylpentene-2, trans-hexene-3, 2-ethylbutene-1, 2-ethylhexene-1, and 2,3-dimethylbutene-2 were obtained from Aldrich Chemical Company, Inc. Acetylene and allene were purchased from Matheson Company, Inc. All other gaseous and liquid hydrocarbon standards were obtained from Phillips Petroleum Company, Special Products Division. Ethylene dicholoride was obtained from Mallinckrodt Chemical Works.

Three basic column types were prepared. A 4-ft., 0.25-inch o.d., glass column of 5% SE-30 on DMCS-treated Chromosorb G and a comparable column of 0.125-inch o.d. glass were prepared using the procedure given in Part I of this thesis. A 20-ft., 0.25-inch o.d., copper column of 10% SE-52 on DMCS-treated Chromosorb W was prepared by the classical procedure.

Procedures

Operation of fragmentation unit

For all studies reported here, the sample tube was

loaded with carbon wool, assembled, and pre-arced for sixty seconds at 85 to 90 ma. with the switching valve in the "inject" mode. After cooling, the tube assembly was disassembled and a solid sample of approximately 0.10 mg. for the ligand and 0.15 mg. for the complex was weighed onto the carbon wool in the tube on a five-place Ainsworth balance. A small plug of silica wool was placed over the sample and the sample sandwich pressed against the inner surface of the electrode positioned to contact the carbon wool side of the sandwich. The other electrode was then placed in position and the assembly placed in the fragmentation module such that the electrode contacting the carbon wool was the downstream electrode. Carrier gas was allowed to purge the sample tube with the switching valve in the "purge" position. The flow rate through the tube was measured with a soap bubble flowmeter to insure that the flow rate was not so high as to allow fragmentation products to escape the sample loop under the chosen discharge conditions. After setting the discharge time and the voltage and allowing sufficient time to purge the system of air and/or solvent, the discharge was initiated. When the discharge terminated, sufficient time (normally five seconds) was allowed for the carrier gas to sweep the tubing connecting the sample tube to the sample loop and the switching valve was actuated to deposit the fragmentation products contained in the loop onto the head of the analytical column. Normal gas chromatographic separation ensued.

It was found absolutely essential to prohibit any carrier gas leakage about the sample tube. Leakage was found to result in poor discharge current stability (fluctuation of current about its mean during a given discharge) and reproducibility (agreement of mean current from discharge to discharge). Sample sizes much in excess of 0.20 mg. were also found to effect stability and reproducibility. Table 11 demonstrates these influences and the current behavior that accompanied the work reported in this thesis.

Table 11. Discharge current stability and reproducibility

Conditions	Relative standard deviation (%) Stability	Reproducibility
Given sample tube	1.8	0.6
Tube to tube	---	2.9
Tube with leak	4.2	10.7
Tube with 0.1 mg. sample	1.5	2.4
Tube with 0.2 mg. sample	1.9	2.3
Tube with 0.3 mg. sample	4.9	6.4

It was found that the deposition of solutes from solution is possible. Solutions, several microliters in size, were deposited on the carbon wool, the solvent driven off in the valve compartment, and the residue fragmented with acceptable results. Celite coated with sample has also been used.

Data treatment

Retention behavior was measured in terms of retention distances using an engineering rule calibrated with forty divisions to the inch. Retention was measured from the point

of injection or from the initial retention distance of methane. All retention parameters correspond to peak-retention.

Peak areas were determined with a Disc Integrator. One "disc unit" of area corresponds to one-hundredth of a single sweep of the integrator pen at maximum detector sensitivity (area equals disc units counted times the detector attenuation). Peak heights were measured to the nearest 0.5% of full-scale. Both peak heights and peak areas were corrected for background.

Discharge "severity" was defined as the reading of the variac setting (in per cent) multiplied by the resulting current in milliamperes. Since the maximum voltage is 3500 volts, the discharge severity may be converted to watts by multiplication by 0.035.

Average relative abundance (ARA) values were determined by dividing the peak area of the component of interest by the total peak area of the pattern to yield peak area-ARA or by using peak heights to obtain peak height-ARA. A measure of the reproducibility of ARA values is given in Table 12. Although the reproducibility of this parameter is much lower than desired*, no better method of treating the data was found.

Peak height-ARA was used extensively because of the ease with which it may be computed. Peak area-ARA values were not

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*This poor reproducibility is most likely the result of this attempted application of the Beckman fragmentation system and not a characteristic of the unit.

found to improve the reproducibility of the data or to result in ARA dependences differing from those found using peak heights. The primary disadvantage of peak height-ARA is that it is not physically meaningful.

Table 12. Precision in the determination of the peak height-average relative abundance of 3,3-dimethylbutene-1 in the ambient column temperature fragmentation patterns for MNDPO and MNDPO-U

Sample	ARA $\pm \sigma$	Rel. std. dev. (%)
MNDPO (solid)	3.9 $\pm$ 1.1	28
MNDPO on celite	3.2 $\pm$ 0.7	22
MNDPO from solution	2.2 $\pm$ 0.6	27
MNDPO-U (solid)	9.7 $\pm$ 1.9	20

Studies

The programmed temperature patterns were obtained with the 0.125-inch o.d. column at a carrier gas flow rate of 22 ml./min. and the temperature-time profile of Figure 12. Sample sizes of 0.10 mg. for the ligand and 0.15 mg. for the complex were employed when weighing was possible. Sample sizes were estimated for MEBDPO, MEHDPO, and MHDPO until fragmentation patterns comparable in size to the others were obtained. A discharge setting of 30% resulting in a current of approximately 60 ma. was used for all of the samples. The discharge time was 30 seconds and the valve compartment was maintained at a temperature of 270°C. Retention positions of the diphosphine oxides, methyl di-n-hexylphosphine oxide and

tri-n-hexylphosphine oxide were obtained by injection of these compounds and chromatographing them under conditions identical to those employed for separating the fragmentation products of the diphosphine oxides.

The C_1-C_6 fragmentation patterns (those patterns containing only the one- to six-carbon fragments; also termed "ambient column temperature fragmentation patterns") were obtained with the 20-ft., SE-52 column operating at air-dump temperature (slightly below ambient) with a carrier gas flow rate of 120 ml./min. Discharge conditions were the same as those for the programmed temperature patterns with the exception that the valve compartment was maintained at 100°C. Sampling procedures were the same as those for the programmed temperature study. Comparison standards (hydrocarbons) were prepared by mixing equal volumes of liquid standards and bubbling the desired gaseous standards into the appropriate mixture. The standard chromatograms presented were synthesized by superimposing the peaks obtained on injection of various standard mixtures which were chromatographed under conditions identical to those employed for the separation of the products of fragmentation of the diphosphine oxides. The method of retention index calculation is given in the Appendix.

The C_1-C_4 region of fragments was examined using the same conditions as were used for the C_1-C_6 region except that the column was operated at 0°C with the aid of the sub-ambient

temperature module. The standard chromatogram was synthesized from peaks obtained on injection of gaseous samples ("gas-tight" syringe) of the hydrocarbons.

The column, column operating conditions, and sampling procedure used in the C_1-C_6 pattern studies were also used in those studies involving the dependence of ARA values on discharge severity, discharge time, flow rate, and enhanced secondary breakdown conditions. The same column, but operated at 80°C , was employed in the internal standard "canceling" study (Table 18).

Studies involving the areas and the shapes of direct-to-detector traces were carried out by swagelocking the exit-line of the sample tube directly to the detector. The necessary carrier-to-fuel ratio was maintained by the use of the carrier gas make-up line. The influence of discharge severity and of discharge time on the total areas of fragmentation patterns was studied using this technique.

The calibration curve given for the quantitative determination of MNDPO using MEBDPO as the internal standard was obtained by depositing the MNDPO and MEBDPO onto the carbon wool from dichloroethylene (4 μl. samples). The 20-ft. column was operated under conditions identical to those employed in the investigation of the C_1-C_6 region of fragments but with a fragmentation time of 20 seconds and discharge voltage setting of 35% (resulting current = 80 milliamperes).

INVESTIGATIONS AND RESULTS

The qualitative behavior of the diphosphine oxides and the uranyl nitrate-diphosphine oxide complexes upon fragmentation was investigated primarily to find whether complexation exerts any effect on the fragmentation patterns. The investigations also yield information concerning the general mode of degradation of the diphosphine oxides and allows an assessment of the value of the technique as a qualitative analytical tool for the diphosphine oxides. Programmed column temperature and ambient column temperature fragmentation patterns were obtained for all seven ligand, metal-ligand pairs. Sub-ambient column temperature patterns were obtained for MNDPO, MNDPO-U, EHDPO, PHDPO, and BHDPO. Quantitative studies of the influence of the operating parameters on the fragmentation of the ligand and the complex, an interpretation of the fragmentation data and an assessment of the potential of fragmentation-gas chromatography as an inorganic analytical tool conclude this section of the thesis.

Qualitative Breakdown Patterns

Programmed temperature patterns

Obtaining fragmentation patterns which include the high-boiling degradation products requires that the temperature of the valve compartment be maintained sufficiently high (270°C) to allow these products to reach the analytical column. As a

result, the reproducibility of the peak sizes is diminished probably because of pre-fragmentation volatilization of the sample and an increased chance of undegraded diphosphine oxide leaving the discharge zone during fragmentation. Because of this diminished reproducibility of the pattern sizes and the fact that the high temperatures may alter the complexes prior to controlled fragmentation, quantitative correlations of these fragmentation patterns with complexation influences are subject to serious error.

For the diphosphine oxides and corresponding complexes, such patterns are useful only in a qualitative sense. They may be used to obtain a general indication of complexation effects. More important, they can be useful in obtaining an indication of the manner of breakdown and in assessing the value of the technique as a structural confirmation tool for the diphosphine oxides.

The absolute size of the fragmentation patterns and the relative sizes of the peaks within the fragmentation patterns were found to be poorly reproducible. The positions of the peaks in the fragmentation patterns were found very reproducible if chromatographic conditions were held constant. The fragmentation patterns chosen for presentation are those obtained with the slightest change in chromatographic conditions, that is, over the shortest possible period of time. These fragmentation patterns are presented in Figures 13

through 19. Figure 12 shows the program employed superimposed on the breakdown pattern of the EHDPO-U complex. The same program was employed for all of the patterns presented. The numbers below each pattern are the detector attenuations corresponding to the given regions of the chromatograms. To compare absolute peak sizes, each peak area must be multiplied by the attenuation employed.

A comparison of the patterns for the ligands and ligand-metal complexes for MNDPO, EHDPO, PHDPO, and BHDPO indicates no significant effect of complexation on the qualitative aspects of the patterns (on the positions of the peaks and approximate relative sizes of the peaks). Those peaks appearing in one pattern but not the other are generally sufficiently small to make it possible that they were undetected in the particular pattern obtained.

A comparison of the patterns for the ligand and ligand-metal complexes for MHDPO, MEBDPO, and MEHDPO appears to indicate the possibility of a complexation effect for these samples. In view of the bulk of the work carried out, it seems more likely that the differences in the patterns are due to the difficulty in sampling the waxy MHDPO and MEBDPO and the liquid MEHDPO and/or to the impurities in these ligands rather than to complexation.

A comparison of the relative peak sizes in the patterns for the ligands and ligand-metal complexes generally shows

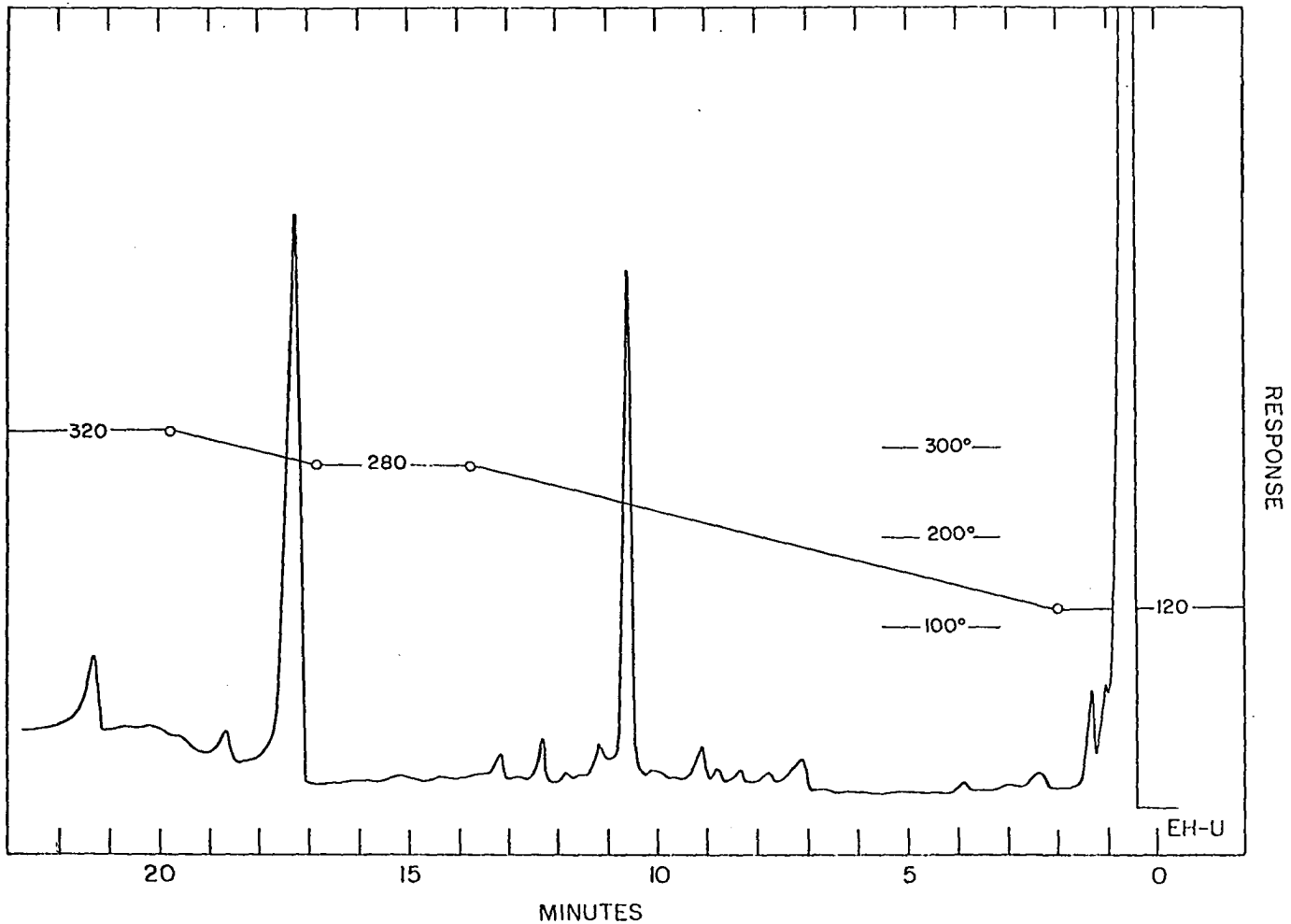

Figure 12. Column temperature program and time-scale of the programmed column temperature fragmentation patterns for the diphosphine oxides

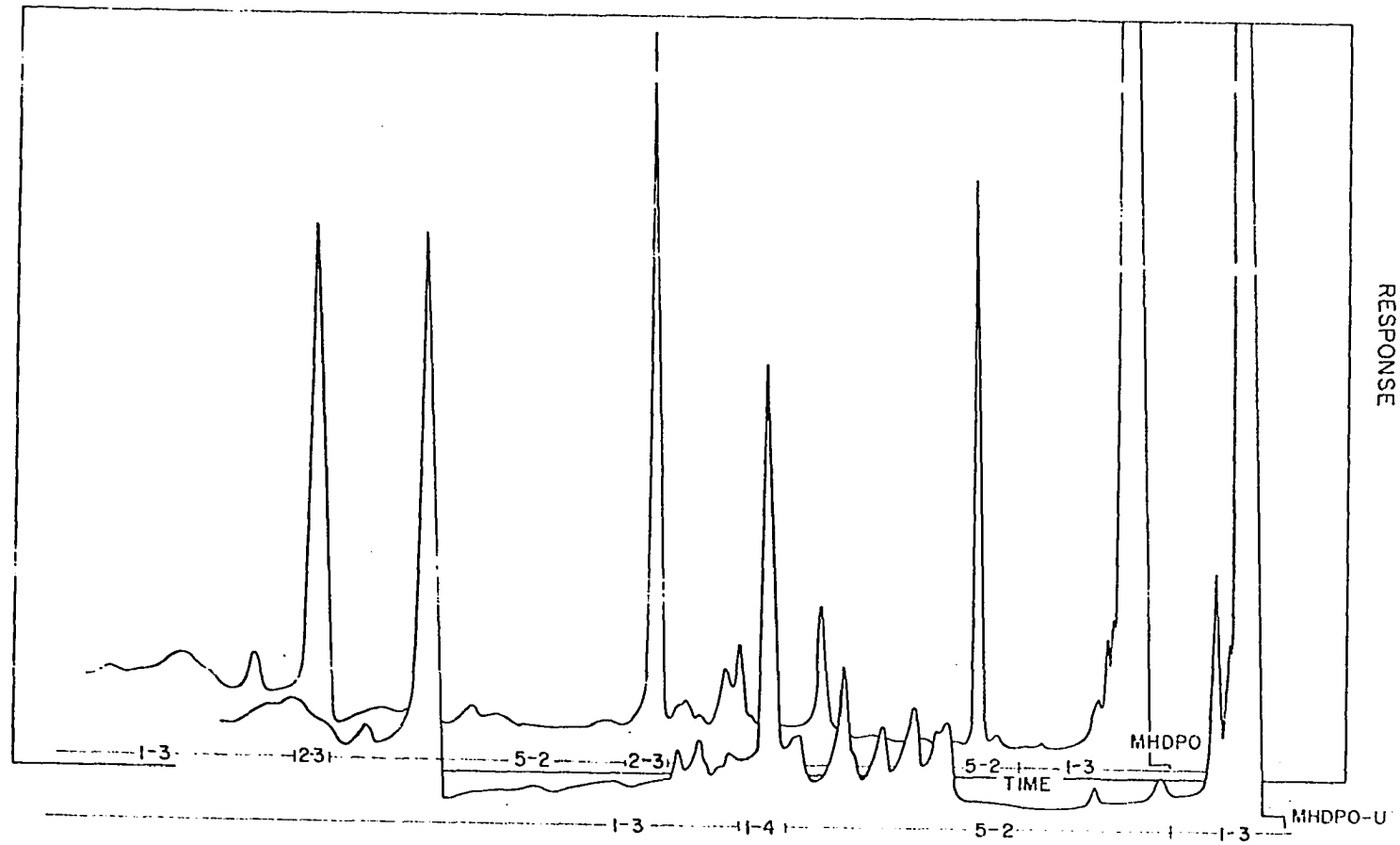

Figure 13. Programmed column temperature fragmentation patterns for MHDPO and MHDPO-U

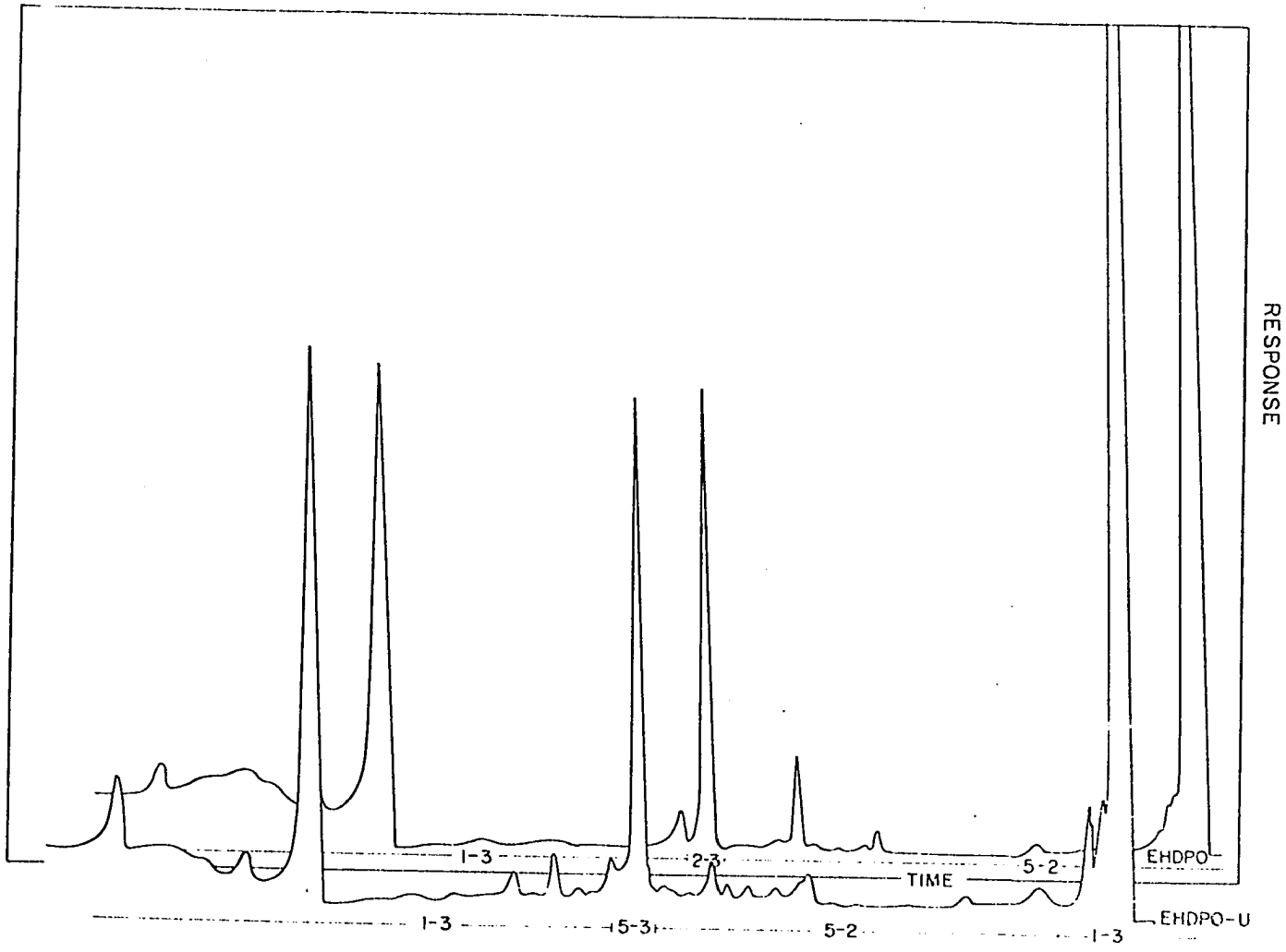

Figure 14. Programmed column temperature fragmentation patterns for EHDPO and EHDPO-U

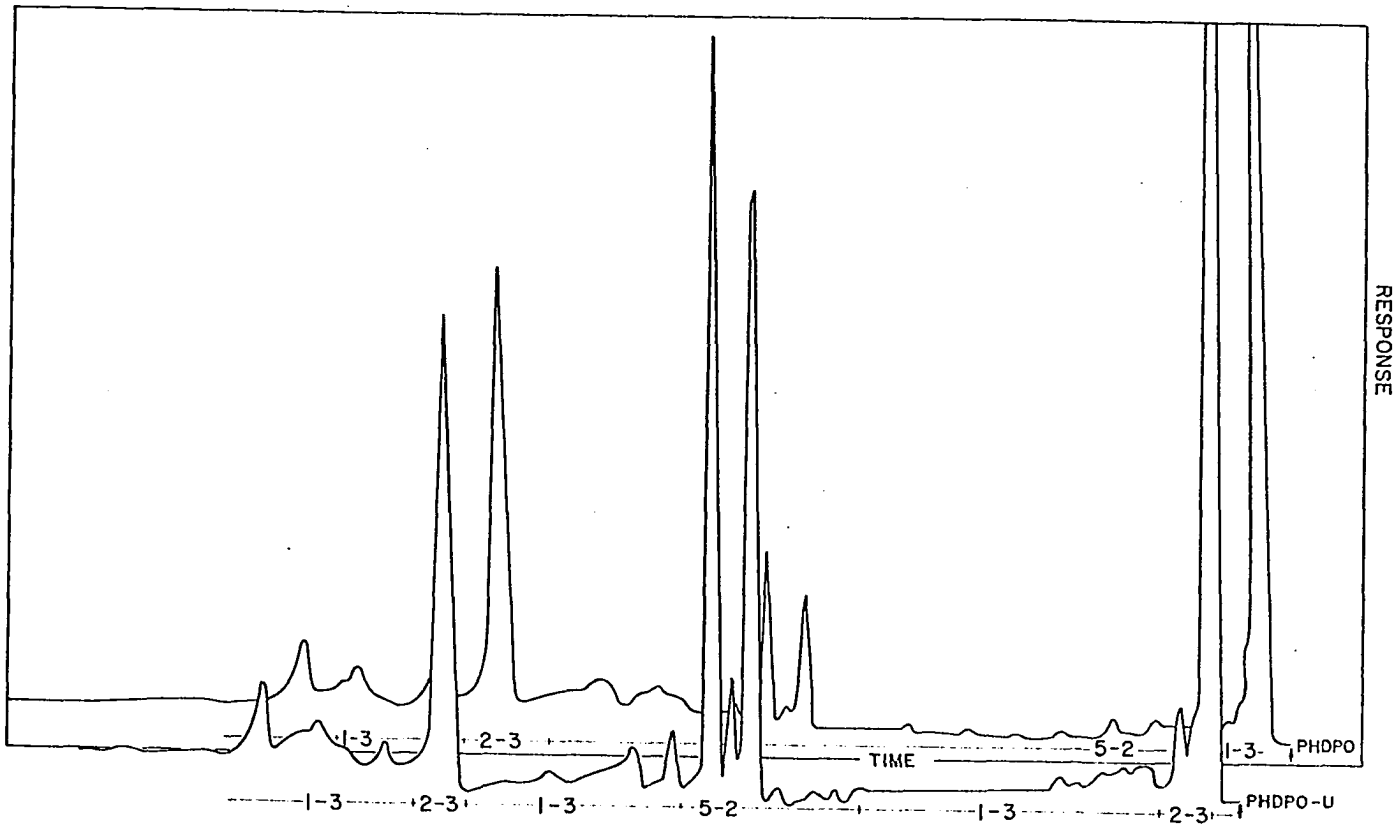

Figure 15. Programmed column temperature fragmentation patterns for PHDPO and PHDPO-U

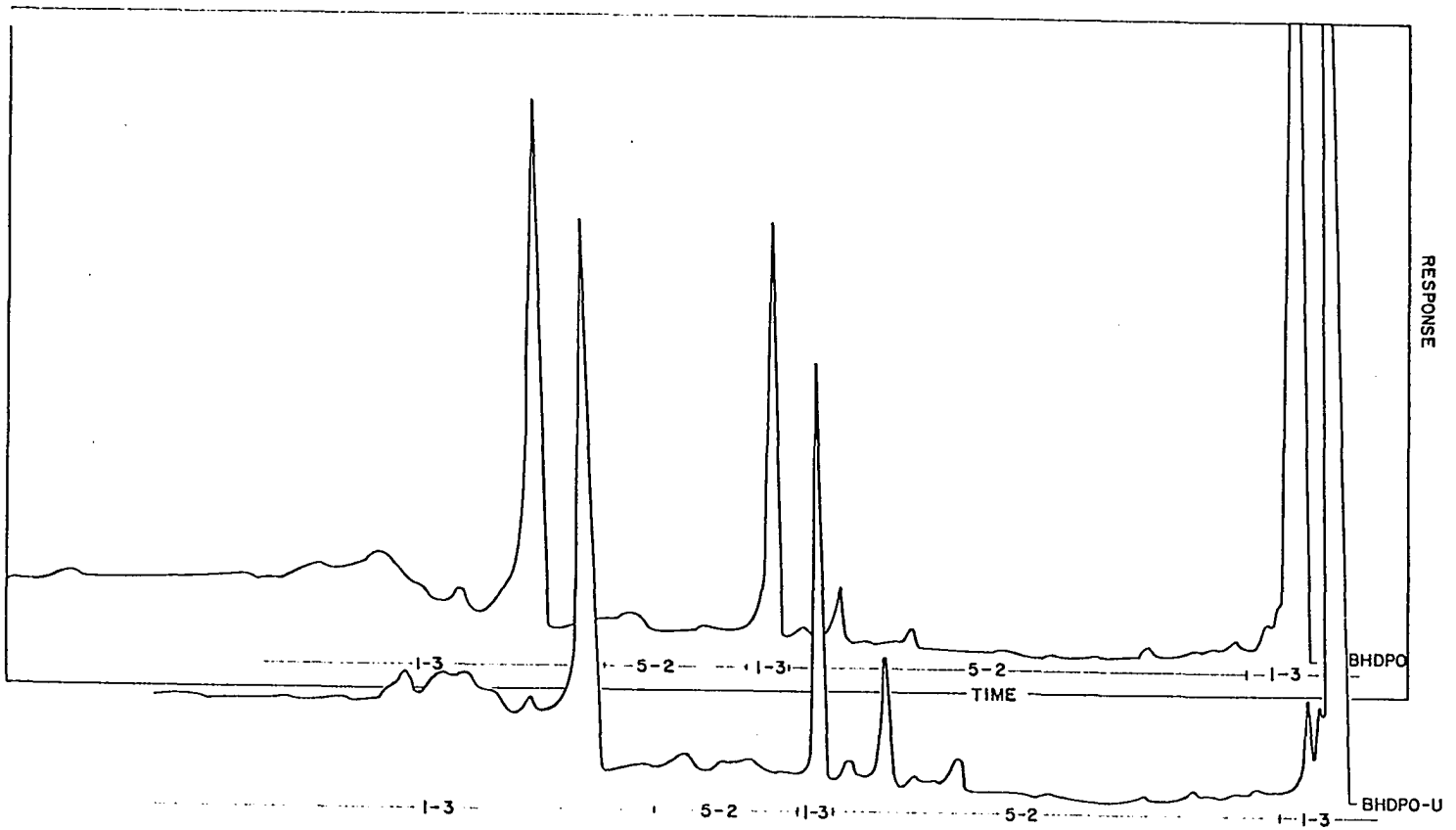

Figure 16. Programmed column temperature fragmentation patterns for BHDPO and BHDPO-U

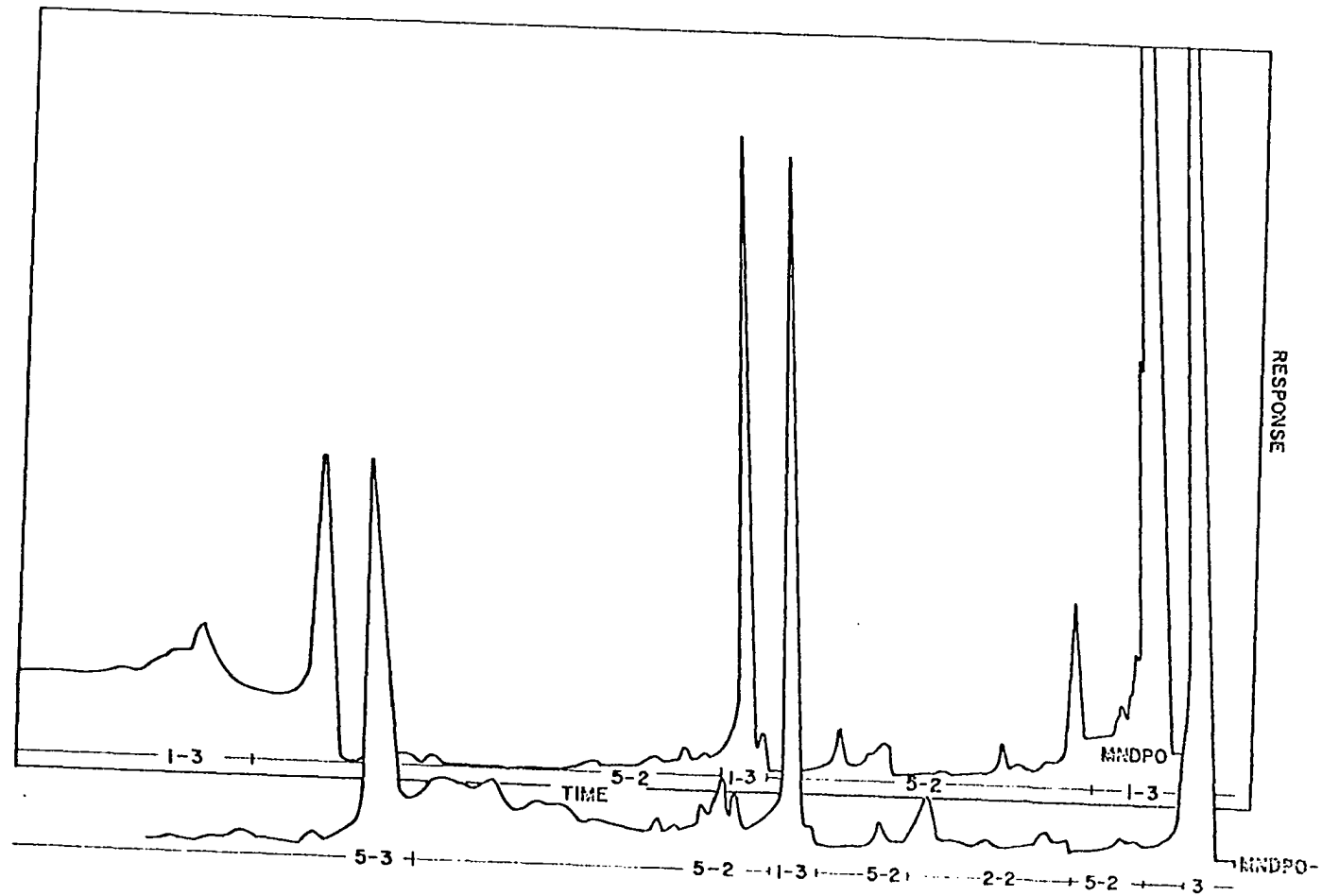

Figure 17. Programmed column temperature fragmentation patterns for MNDPO and MNDPO-U

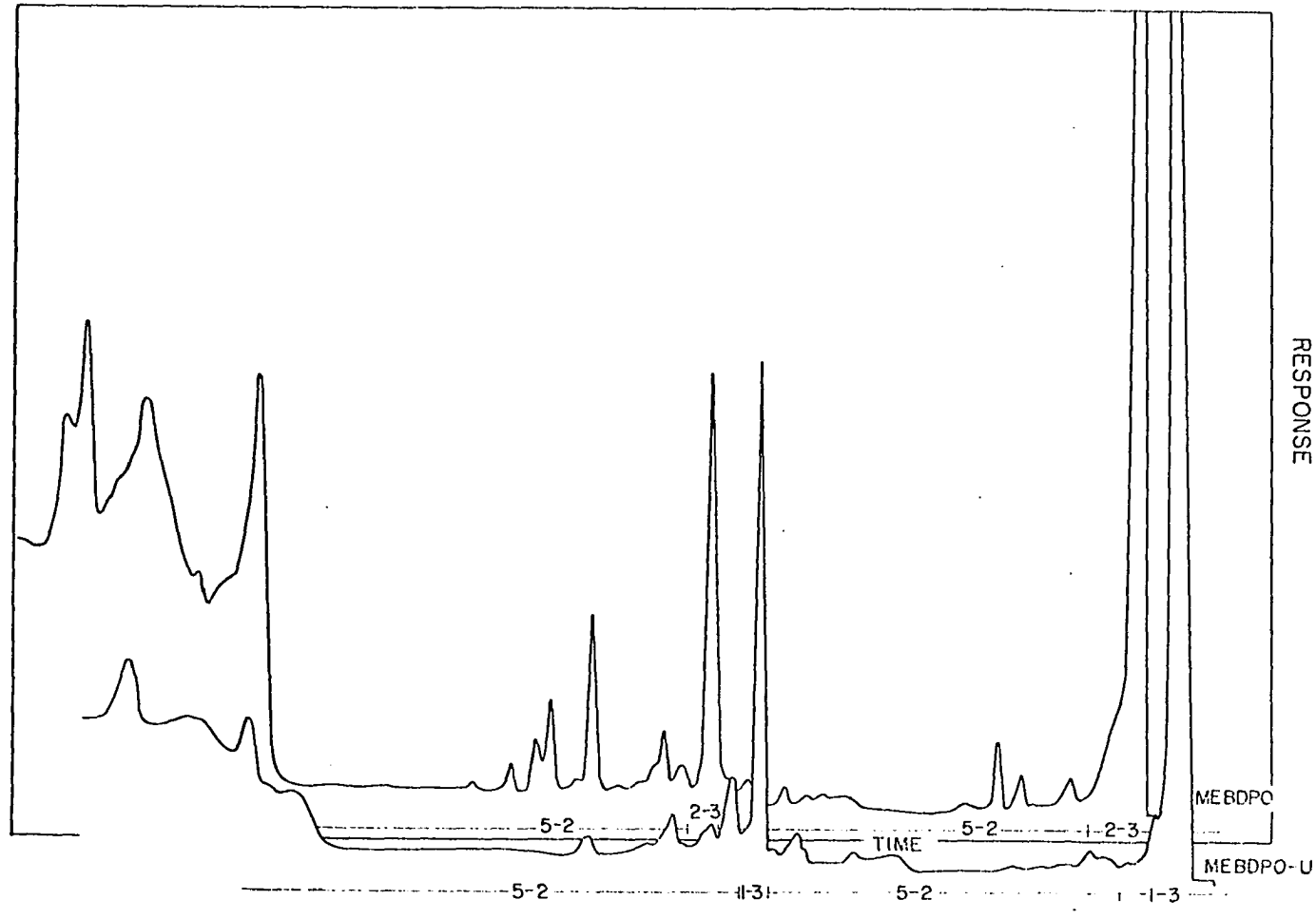

Figure 18. Programmed column temperature fragmentation patterns for MEBDPO and MEBDPO-U

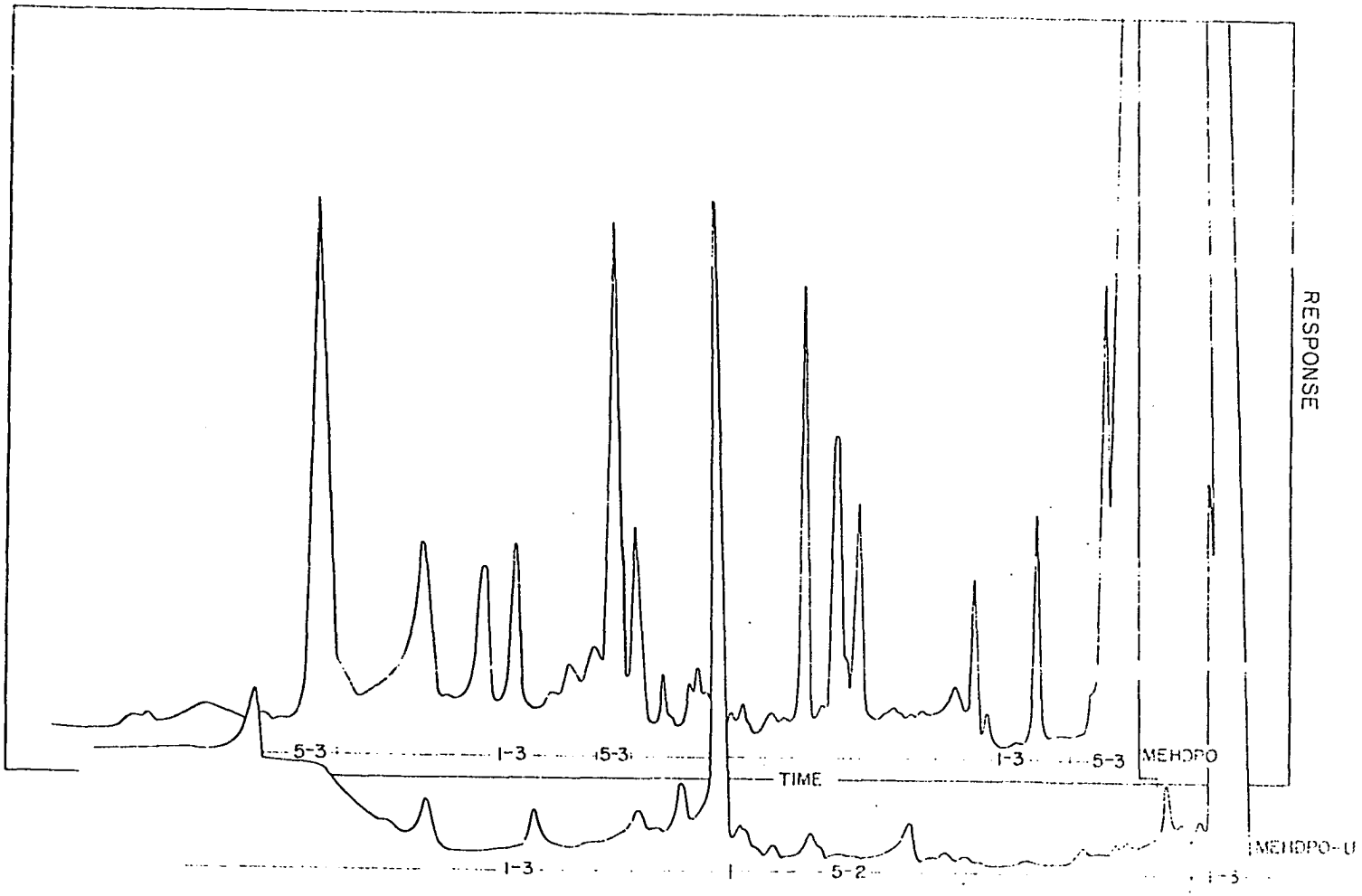

Figure 19. Programmed column temperature fragmentation patterns for MEHDPO and MEHDPO-U

a good number of differences. Many of these differences are small and probably do not reflect influences of complexation. Some are sufficiently large to indicate they are complex-sensitive. The danger of drawing definite conclusions of this type from these patterns has been pointed out.

Although no serious attempt was made to identify the fragmentation products, the regions of the chromatograms where undegraded diphosphine oxide, methyl di-n-hexylphosphine oxide, and tri-n-hexylphosphine oxide emerge were established. The monophosphine oxides were found to emerge in the seventeen to nineteen minute region (see Figure 12) with the diphosphine oxides emerging after twenty minutes. Judging from the chromatographability of organophosphorus compounds (11,23) and using the determined elution positions as a guide, it can be postulated that the earlier emerging peaks may correspond to tertiary alkylphosphine oxides with alkyl substituents of less than six carbons, secondary alkylphosphine oxides, and phosphines. These products might be expected on the basis of the work on the pyrolysis of the monophosphine oxides (5). Although the formation of phosphinic acids is also predicted (5), difficulties encountered in chromatographing di-n-hexylphosphinic acid on the column employed in these studies suggest that phosphinic acids would not appear in the chromatograms.

It is of interest to note that the peaks corresponding

to undegraded diphosphine oxides were not observed. In those cases where peak position agreed with that of the diphosphine oxide, the peak was always very small. This appears to indicate that little, if any, of the sample is volatilized either because of the high temperature of the valve compartment or during fragmentation. Yet, as discussed later, there is significant evidence that volatilization, particularly during fragmentation, does occur.

This behavior might be explained by the fact that, as found in the conventional gas chromatography study, metal inlets and columns result in the decomposition of the diphosphine oxides. Any diphosphine oxide volatilized from the fragmentation tube prior to or during fragmentation must pass through the sample loop before reaching the analytical column. The stainless steel sample loop at 270°C. is, in effect, an unpacked metal column. As such, it would be expected to degrade any diphosphine oxide entering it. It is worthy of note that this uncontrolled decomposition would be expected to further decrease the reproducibility of patterns.

The qualitative (positions and relative sizes of the peaks) differences between the fragmentation patterns of the uncomplexed diphosphine oxides appears to be sufficiently great to allow the use of the technique for the identification of these compounds. Since the diphosphine oxides can be gas chromatographed intact, the practical value of fragmenta-

tion-gas chromatography for their identification is minimal. An interesting potential application of the technique is the identification and quantitative estimation (as shown possible later) of diphosphine oxides on chromatographic supports.

C_1-C_6 fragments

Because only those fragmentation products volatile enough to pass through the valve compartment can reach the analytical column, operation of the valve compartment at a lower temperature (100°C.) imposes a limitation on the type of fragments visible in the fragmentation pattern. It has been found that, typical of the pyrolysis of organophosphorus compounds (5,8, 9,10,65), the diphosphine oxides degrade with the formation of characteristic low-boiling hydrocarbons. As such, the volatility limitation is not serious in the fragmentation-gas chromatography of diphosphine oxides.

The ability to operate at relatively low, constant column temperatures has certain advantages. For one, lower temperatures normally allow higher detector sensitivities as a result of decreased column bleeding. Also, isothermal operation allows a greater confidence in retention data making peak identification easier.

Figures 20 through 26 compare the ambient column temperature fragmentation patterns (those patterns composed of one- to six-carbon fragments) of the diphosphine oxides and corresponding ligand-metal complexes. As for the programmed

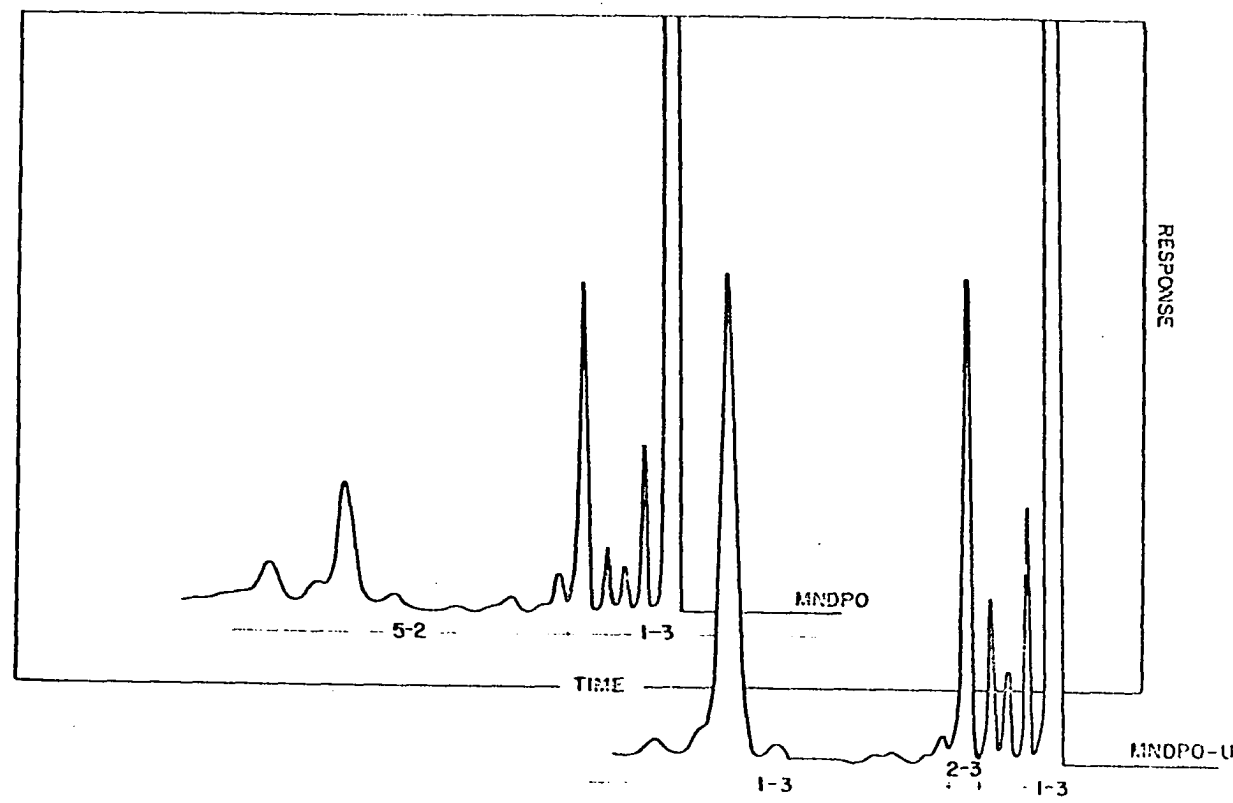

Figure 20. Ambient column temperature fragmentation patterns for MNDPO and MNDPO-U

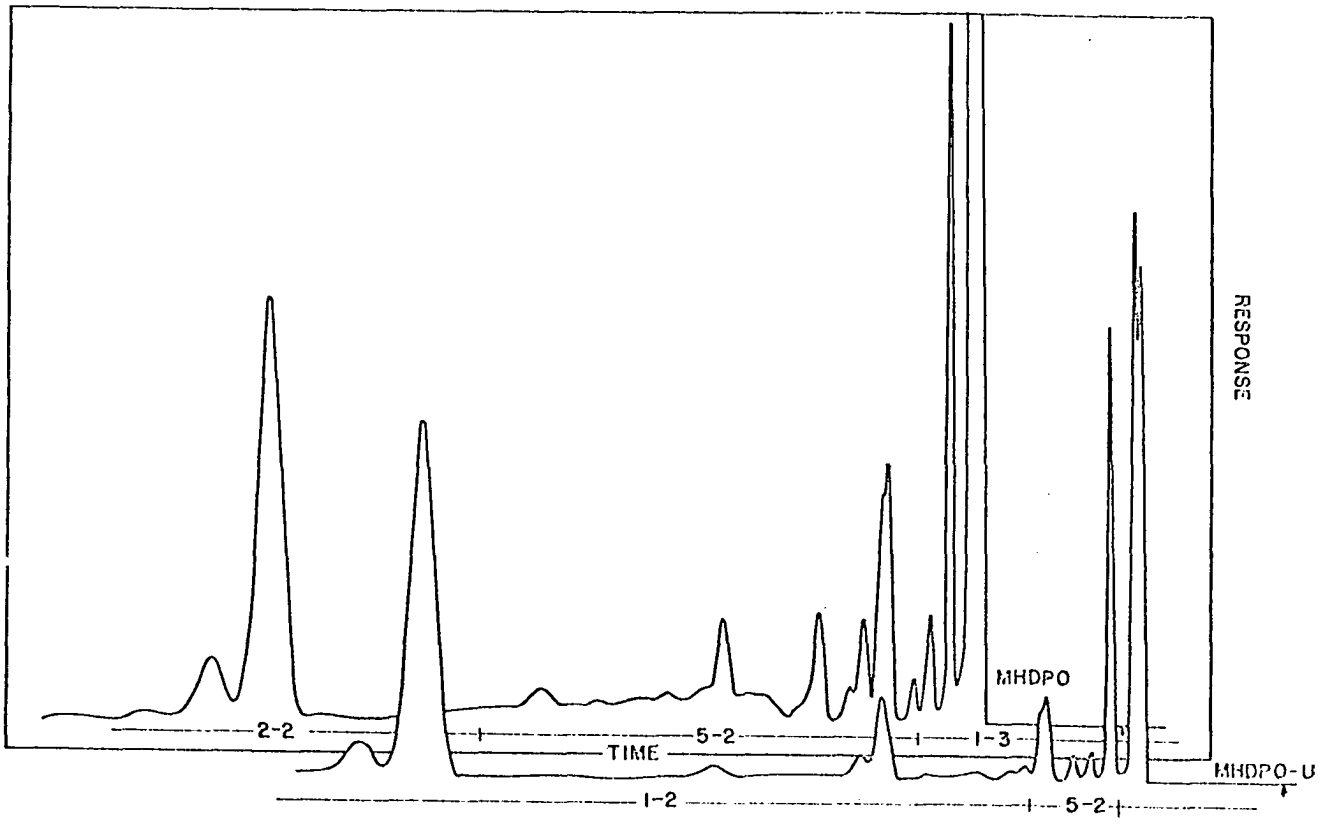

Figure 21. Ambient column temperature fragmentation patterns for MHDPO and MHDPO-U

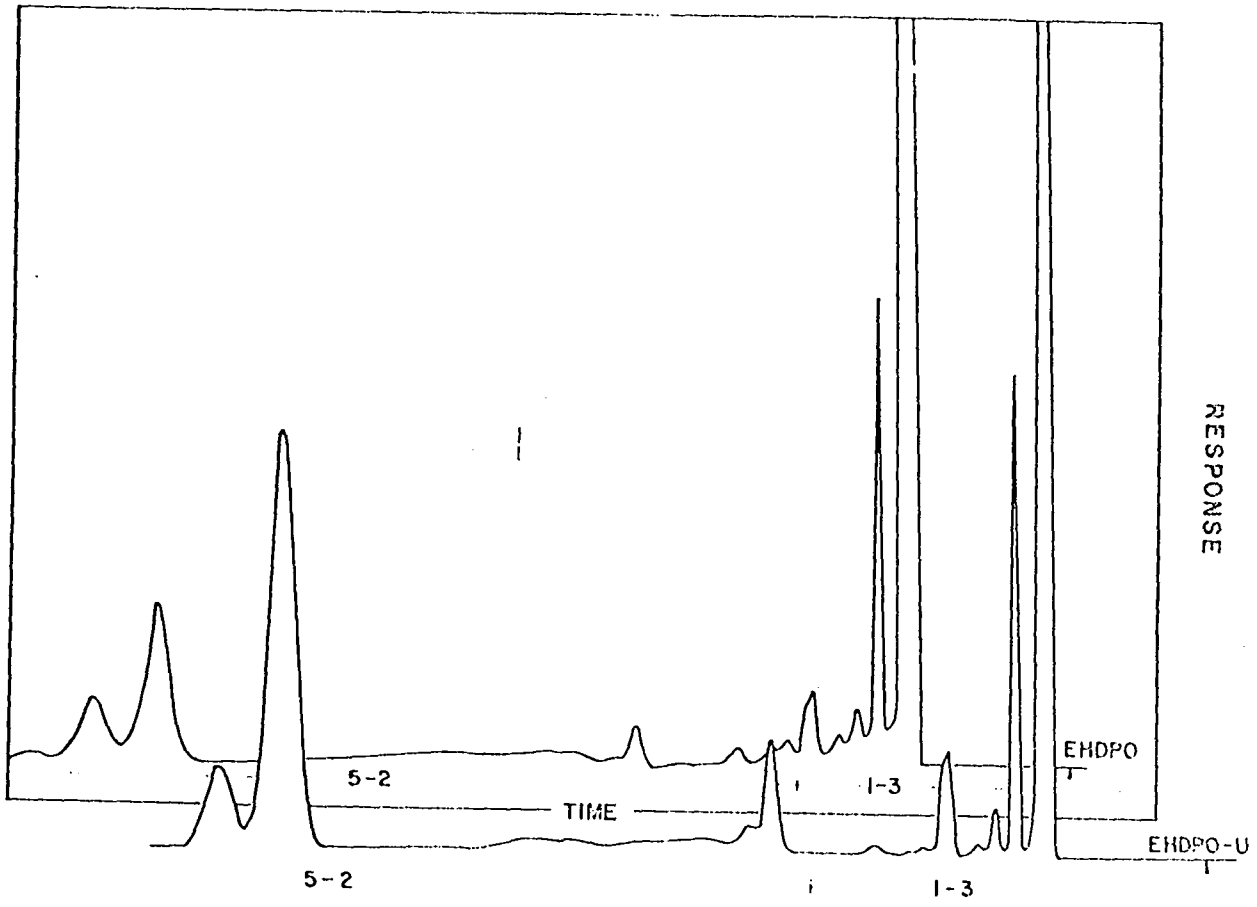

Figure 22. Ambient column temperature fragmentation patterns for EHDPO and EHDPO-U

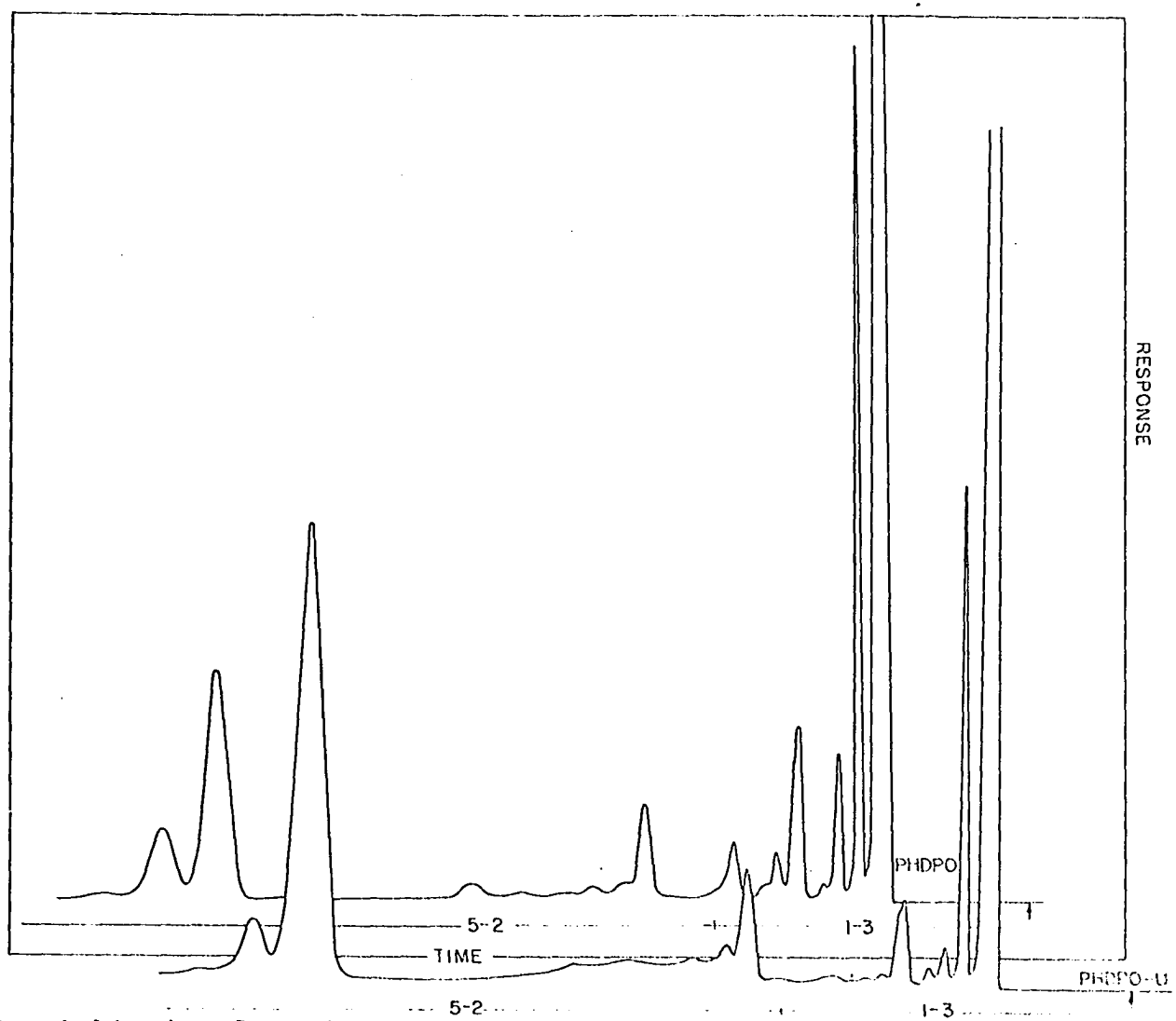

Figure 23. Ambient column temperature fragmentation patterns for PHDPO and PHDPO-U

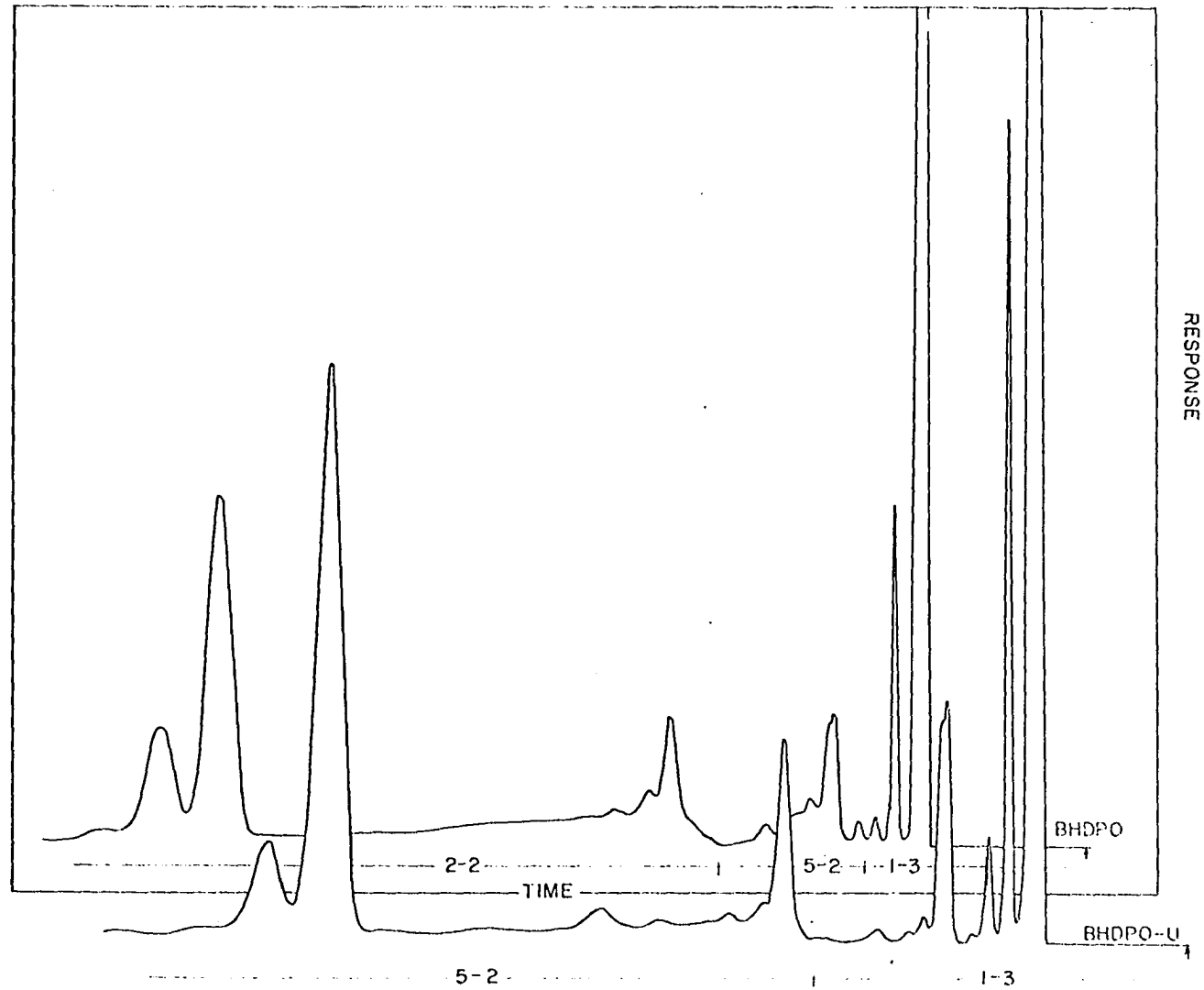

Figure 24. Ambient column temperature fragmentation patterns for BHDPO and BHDPO-U

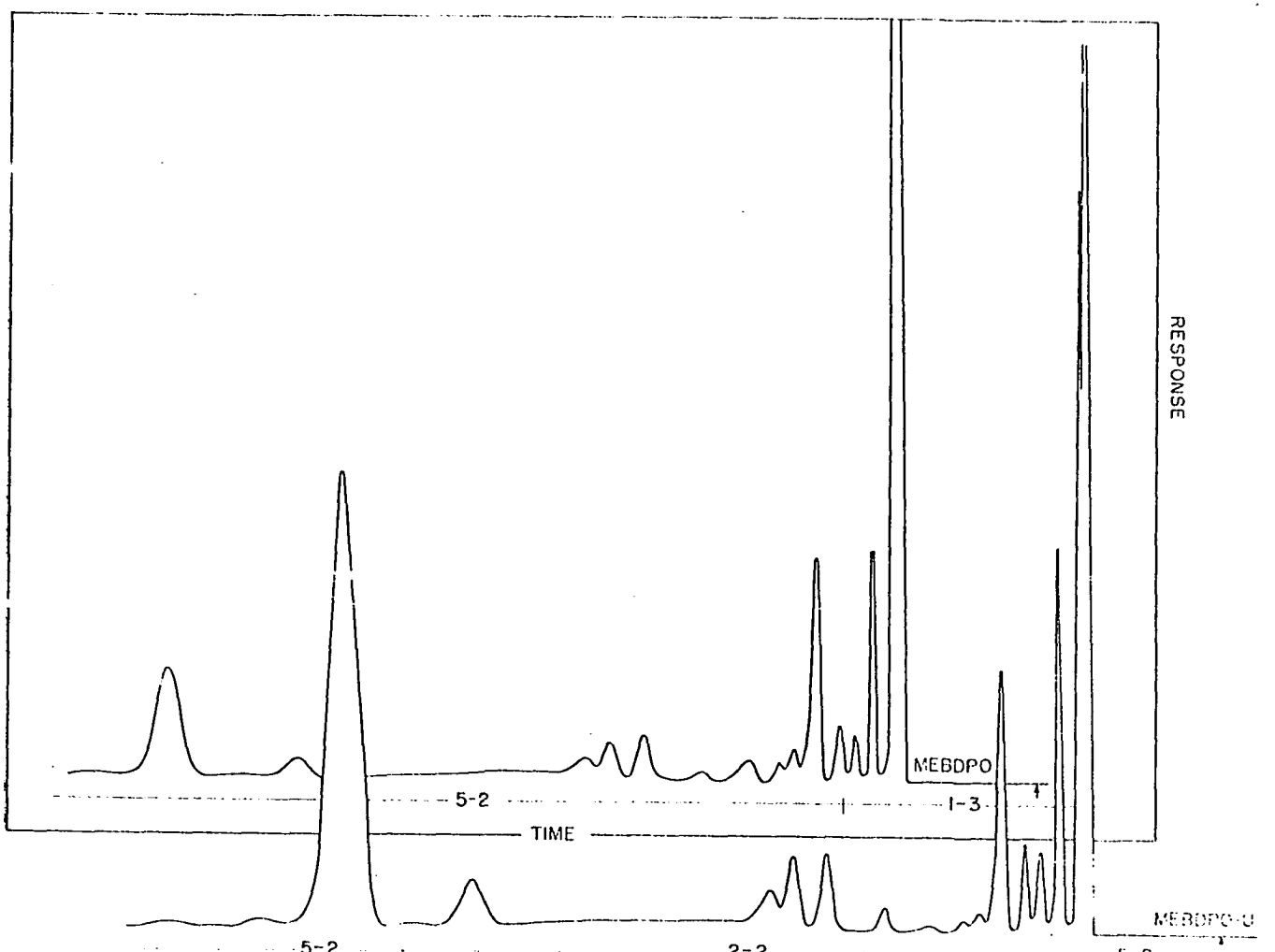

Figure 25. Ambient column temperature fragmentation patterns for MEBDPO and MEBDPO-U

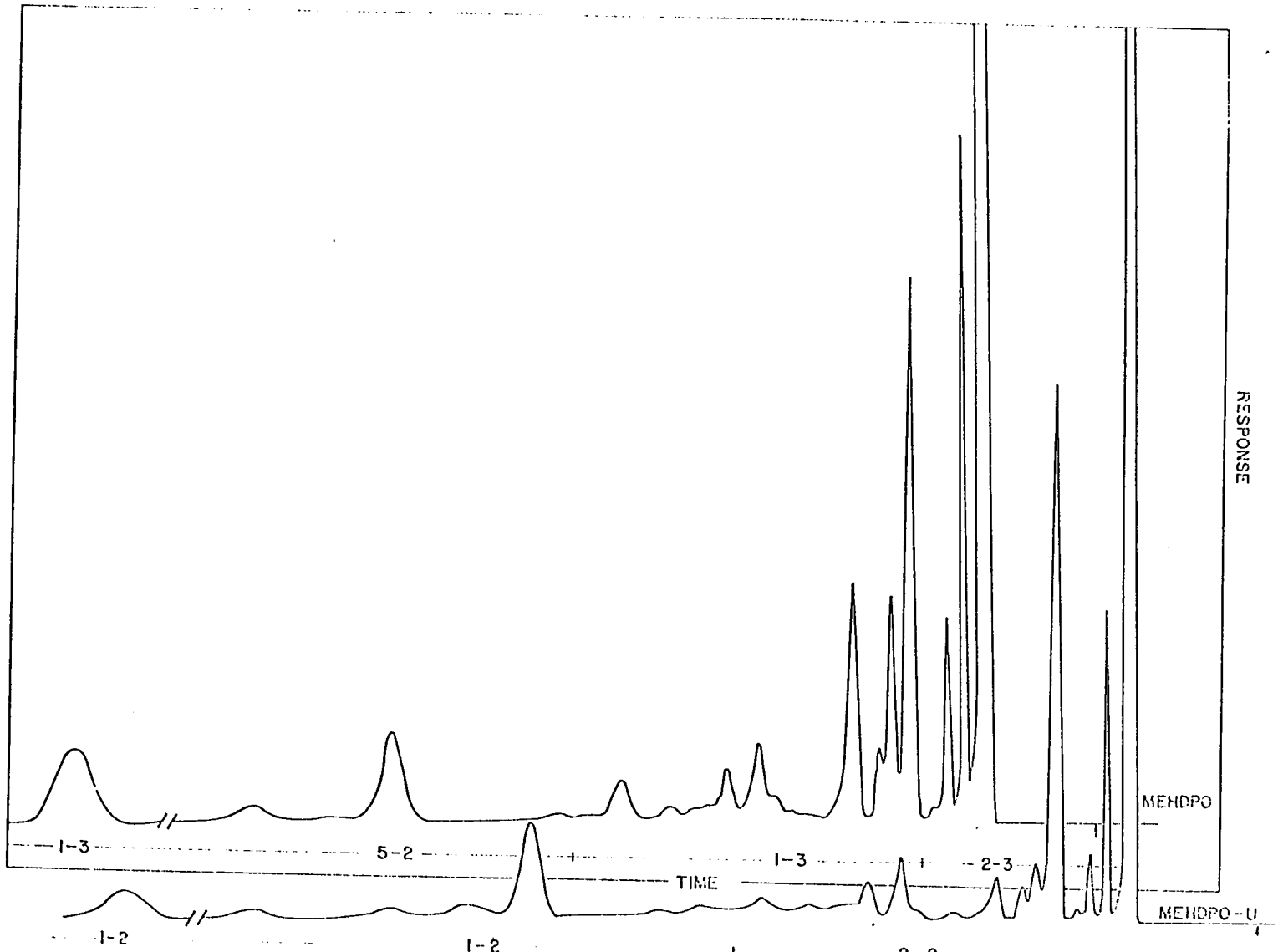

Figure 26. Ambient column temperature fragmentation patterns for MEHDPO and MEHDPO-U

temperature patterns, the numbers below the chromatograms correspond to detector attenuations. The time axis corresponds to that of the C_1-C_6 standard chromatogram (Figure 27). Other operating conditions are given in the "Materials" section, Part II, of the thesis. For reasons analogous to those described for the preceding study, the chromatograms presented are those obtained over the shortest possible period of time.

A comparison of the patterns (Figures 20-26) shows that those from MHDPO, EHDPO, PHDPO, and BHDPO are essentially the same except for absolute size. Similar patterns would be expected because each ligand contains the same alkyl (n-hexyl) group. The lesser similarity of the MHDPO pattern may be due to sampling as is mentioned above for the programmed temperature patterns.

A comparison of the patterns for MNDPO, MEBDPO, and MEHDPO also shows the expected behavior. These patterns are very different from one other and from those of the n-hexyl compounds because each has a different alkyl group. Because the differences are in positions of peaks as well as sizes, it can be concluded that the differences are real and not due to sampling variations.

A visual comparison of the patterns from the ligand and the corresponding ligand-metal complex indicates that complexation does not direct the formation of a significant amount of

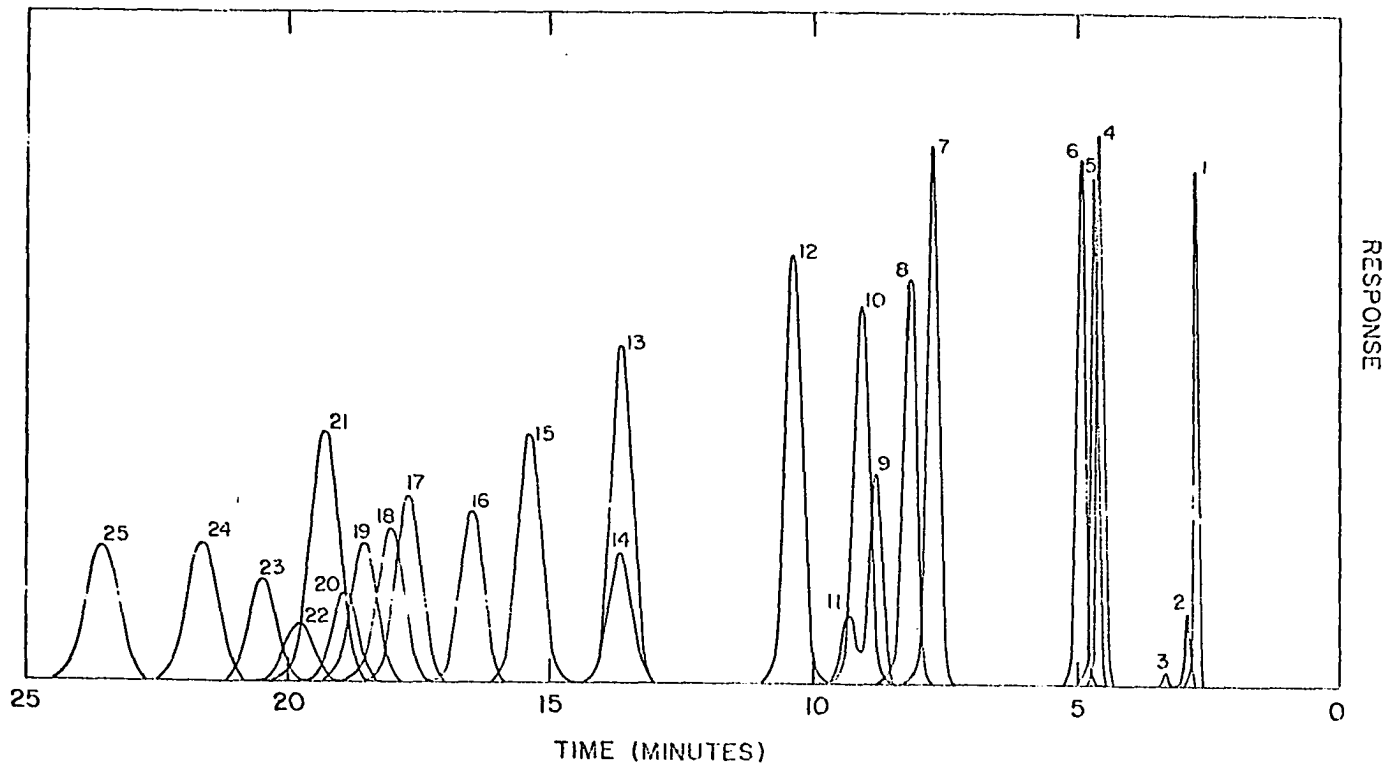

Figure 27. Ambient column temperature standard chromatogram of C_1-C_6 hydrocarbons

Table 13. Peak assignments and retention data for the standard chromatogram of the C_1-C_6 hydrocarbons

No.[a]	Compound	Retention index	Retention time[b] min.	Boiling point[c] °C
1.	Methane	100[d]	2.6	-161.45
2.	Ethane, Ethylene, Acetylene	--	2.9	--
3.	Propane	300[d]	3.3	-42.07
4.	Isobutylene	394	4.1	-6.900
5.	n-Butane	400[d]	4.3	-0.50
6.	Neopentane	413	4.9	9.503
7.	Pentene-1	492	7.6	29.968
8.	n-Pentane	500	8.2	36.074
9.	trans-Pentene-2	510	8.8	36.353
10.	3,3-Dimethylbutene-1	515[e]	9.1	41.247
11.	cis-Pentene-2	518	9.3	36.942
12.	Neohexane	535	10.5	49.741
13.	Cyclopentane	568	13.6	49.262
14.	2-Methylpentane	568	13.6	60.271
15.	3-Methylpentane	583	15.4	63.282
16.	Hexene-1	592[e]	16.6	63.485
17.	n-Hexane	600	17.6	68.740
18.	2-Ethylbutene-1	602	18.1	64.682
19.	trans-Hexene-3	605	18.6	67.088
20.	trans-Hexene-2	607	18.9	67.884
21.	2-Methylpentene-2	609	19.3	67.308
22.	cis-3-Methylpentene-2	613	19.8	67.702
23.	cis-Hexene-2	617	20.5	68.891
24.	trans-3-Methylpentene-2	623	21.6	70.438
25.	2,3-Dimethylbutene-2	632	23.5	73.205

[a]Numbers refer to peak numbers in Figure 27.

[b]Peak retention from the point of injection.

[c]°C at 1 atm (1).

[d]By definition.

[e]Computed using Kovats relation (64).

any product not found in the fragmentation of uncomplexed ligand. Thus, no peaks in a pattern from a mixture of complexed and uncomplexed ligand can be expected to be purely ligand-sensitive or complex-sensitive.

The pattern comparison does, however, indicate that complexation exerts an influence on the relative sizes of many peaks. The two- to four-carbon fragment regions of the patterns seem highly complex-sensitive. This is a dangerous region for quantitative use, however, since most C_4 and smaller fragments probably arise from secondary breakdown. At the least, secondary breakdown contributes significantly to this region. Also, it has been found that, at attenuations of 2-2 (1/200 of the maximum detector sensitivity) and lower, a noticeable contribution is made to the C_1-C_3 region by the carbon wool used in sample loading (this behavior persists even after two sixty-second discharge pre-arcings of maximum severity). In agreement with expectations, relative peak sizes in this region have been found poorly reproducible.

A closer examination of the patterns shows a significant influence of complexation on the sizes of the peaks corresponding to the "characteristic" 1-olefins (those expected on the basis of the pyrolysis of tertiary alkylphosphine oxides (5)) relative to the total sizes of the patterns. Among the patterns presented, this effect is especially apparent for MEBDPO (Figure 25). It may also be seen in the patterns for

MNDPO (Figure 20) and EHDPO (Figure 22). The "characteristic peak" (that corresponding to the characteristic 1-olefin) may be readily recognized by the fact that, for every pattern other than MEHDPO, it is the largest peak to appear after eight minutes (Figure 27). For MEHDPO, the characteristic peak is the last to emerge.

The area-relative abundance of the characteristic 1-olefin was computed by dividing the area of the characteristic peak by the total area of the pattern exclusive of the off-scale methane-ethane region. Because the area of the peaks is proportional to the weight of the hydrocarbons causing the peaks and the detector response is independent of the minor variations in the structures of the hydrocarbons, the area-relative abundance is also the weight per cent of the products in the C_3-C_6 fragment region being characteristic 1-olefin. The area-relative abundances for the patterns of Figures 20 through 26 are presented in Table 14.

Table 14. Area-relative abundances of the characteristic 1-olefins in the ambient column temperature fragmentation patterns for the complexed and uncomplexed diphosphine oxides

Diphosphine oxide	Area-relative abundance	
	Uncomplexed	Complexed
MHDPO	0.20	0.46
EHDPO	0.26	0.42
PHDPO	0.22	0.41
BHDPO	0.28	0.37
MNDPO	0.10	0.41
MEBDPO	0.26	0.71
MEHDPO	0.12	0.03

In each case, except for MEHDPO, the area-relative abundance of the characteristic peak is seen to be significantly greater for complexed than for uncomplexed ligand. Repeated tests of the MEHDPO pair showed the area-relative abundance to be larger for complexed than uncomplexed diphosphine oxide by a factor of about two. The reverse behavior seen in Figure 26 and Table 14 is probably a sampling effect.

Repeated consideration of this behavior for MNDPO, EHDPO, PHDPO, and BHDPO continually resulted in a larger average abundance (using peak heights in this case) for the characteristic peak from the fragmentation of the complexed ligand than uncomplexed ligand. The average of seven runs was employed to determine the peak height-average relative abundance of the characteristic peak from the fragmentation of MNDPO and MNDPO-U presented in the "Materials" section (Part II). Because this behavior was consistent and the most reproducible, the ARA of characteristic peak was chosen as the complex-sensitive parameter to evaluate the potential of fragmentation-gas chromatography as an inorganic analytical tool.

The fragmentation patterns of Figures 20 through 26 may also be presented in tabular form. This is done in Table 15 in terms of the retention index* (35,64) and area of each peak.

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*The origin of the relation used to compute retention indices, method of computation, and advantages of the computation scheme and retention index system are considered in the Appendix.

Table 15. Tabular presentation of the C_3-C_6 portion of the ambient column temperature fragmentation patterns for the diphosphine oxides and uranyl nitrate-diphosphine oxide complexes

Apparent retention index[a] - area[b]				
MHDPO	MHDPO-U	EHDPO	EHDPO-U	PHDPO
310 - 46.0	310 - 6.6	303 - 32.0	307 - 35.0	299 - 60.0
341 - 8.0	341 - 0.8	341 - 5.0	344 - 5.0	339 - 16.0
360 - 2.5	366 - 0.7	368 - 2.0	368 - 2.0	365 - 2.0
394 - 11.5	396 - 1.6	396 - 4.0	398 - 10.0	396 - 16.0
400 - 10.5	400 - 1.4	401 - 3.0	401 - 8.0	401 - 14.0
415 - 6.5	415 - 0.3	417 - 1.0	418 - 2.0	417 - 6.5
428 - 2.3	428 - 0.2	428 - 1.0	449 - 3.0	427 - 3.0
447 - 9.0	492 - 1.5	449 - 1.5	493 - 10.5	447 - 12.0
492 - 6.0	500 - 0.5	493 - 3.5	501 - 2.5	492 - 8.0
499 - 1.5	592[c] - 12.6	502 - 1.0	592[c] - 66.0	500 - 2.0
511 - 1.0	600 - 1.2	592[c] - 23.6	600 - 12.5	512 - 1.5
545 - 3.5		600 - 10.6		545 - 3.5
592[c] - 29.0		607 - 1.2		592[c] - 44.0
600 - 4.8				600 - 15.0
PHDPO-U	BHDPO	BHDPO-U	MNDPO	MNDPO-U
303 - 40.0	299 - 26.0	308 - 62.0	300 - 12.0	300 - 20.0
343 - 4.5	338 - 4.0	342 - 11.0	341 - 5.0	339 - 9.0
368 - 3.0	365 - 1.8	367 - 1.5	366 - 6.5	366 - 15.0
396 - 8.0	394 - 4.3	397 - 22.0	394 - 36.0	393 - 94.0
400 - 7.0	398 - 3.8	400 - 19.5	414 - 32.5	415 - 4.0
414 - 1.0	414 - 2.0	416 - 4.0	430 - 1.0	428 - 1.0
429 - 0.5	426 - 1.0	430 - 2.0	448 - 0.5	449 - 1.0
449 - 1.5	446 - 1.5	448 - 3.0	499 - 0.8	460 - 0.8
475 - 0.5	492 - 4.0	492 - 16.5	515[c] - 11.5	498 - 5.0
493 - 6.2	500 - 1.4	500 - 2.0	523 - 2.0	515[c] - 115.0
500 - 1.5	511 - 8.0	511 - 1.0	535 - 5.0	522 - 7.0
511 - 0.6	592[c] - 23.5	531 - 0.8		535 - 6.0
531 - 0.6	600 - 8.1	544 - 4.0		
545 - 0.6		592[c] - 98.0		
592[c] - 58.3		600 - 18.0		
599 - 7.1				

[a]Retention distances from methane rather than air.

[b]Peak area in disc units $x10^{-4}$.

[c]Reference peak for retention index computation.

Table 15. (Continued)

Apparent retention index[a] - area[b]			
MEBDPO	MEBDPO-U	MEHDPO	MEHDPO - U
302 - 19.0	304 - 6.2	301 -108.0	300 - 14.0
341 - 5.0	341 - 1.8	340 - 52.0	339 - 4.0
366 - 3.0	366 - 1.8	367 - 4.0	365 - 1.0
395 - 12.0	396 - 5.6	395 - 54.0	394 - 10.0
402 - 4.0	401 - 2.0	402 - 48.0	401 - 8.2
416 - 2.5	416 - 0.6	415 - 34.0	414 - 2.0
428 - 1.5	429 - 0.4	428 - 11.0	427 - 1.2
449 - 2.5	450 - 0.4	448 - 46.0	448 - 2.0
476 - 1.3	475 - 1.0	493 - 4.0	475 - 0.4
500 - 5.0	499 - 3.4	499 - 17.0	492 - 0.4
512 - 4.5	511 - 3.3	512 - 12.0	499 - 2.8
519 - 3.0	518 - 2.4	519 - 0.5	511 - 1.8
583 - 5.0	583 - 4.0	522 - 1.0	545 - 1.1
602[c]- 24.5	602[c]-100.0	531 - 3.0	592[d]- 4.1
	612 - 3.5	545 - 13.0	602 - 0.7
	617 - 3.0	592[d]- 21.5	613 - 0.4
		613 - 6.5	629 - 0.7
		664 - 62.0	664 - 2.0

[d]Assumed to be hexene-1 and used as reference for retention index computation.

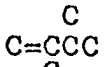
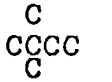
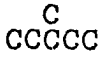
Certain advantages accompany such a presentation. Noting exact peak positions and sizes makes meaningful comparisons of patterns easier. More important, presentation of peak positions in terms of retention indices offers a valuable means of identifying peaks.

Table 16 summarizes the breakdown products assigned to various peaks in the ambient column temperature fragmentation patterns of the seven diphosphine oxides. Because the metal-ligand complexes form the same products on fragmentation as do the ligands, the assignments of Table 16 are equally valid

Table 16. Peak assignments for the C_3-C_6 portion of the ambient column temperature fragmentation patterns for the diphosphine oxides

Fragment	Peak retention index						
	MHDPO	EHDPO	PHDPO	BHDPO	MNDPO	MEBDPO	MEHDPO
CCC/C=CC	310	303	299	299	300	302	301
C=C=C	341	341	339	338	341	341	340
$\begin{matrix} & C & \\ C & C & C \end{matrix}$	360	368	365	365	366	366	367
$\begin{matrix} & & C \\ C=C & & C \\ & C & \end{matrix}$	394	394	396	394	394	394	395
CCCC/C=CC=C	400	401	401	400	---	402	402
t-CC=CC/$\begin{matrix} & C & \\ C & C & C \\ & C & \end{matrix}$	415	417	417	414	414	416	415
c-CC=CC	428	428	427	426	430	428	428
$\begin{matrix} & C & \\ C & C & C \end{matrix}$	447	449	447	446	448	449	449
CCCC=C	492	493	492	492	---	---	493
CCCCC	499	502	500	500	499	500	499
t-CCC=CC	511	---	512	511	---	512	512
$\begin{matrix} & & C & \\ C & = & C & C \\ & & C & \end{matrix}$	---	---	---	---	515	---	---
c-CCC=CC	---	---	---	---	---	519	519

Table 16. (Continued)

Fragment	Peak retention index						
	MHDPO	EHDPO	PHDPO	BHDPO	MNDPO	MEBDPO	MEHDPO
	---	---	---	---	523	---	---
	---	---	---	---	535	---	---
	---	---	---	---	---	583	---
CCCCC=C	592	592	592	592	---	---	592
CCCCCC	600	600	600	600	---	---	---
CCC(=C)CC	---	---	---	---	---	602	---

for the corresponding fragmentation patterns for the complexes.

Not all assignments can be made with equal confidence. The most confident assignment is that of the characteristic peak (I, MHDPO, EHDPO, PHDPO, BHDPO = 592; I, MNDPO = 515; I, MEBDPO = 620; I, MEHDPO not given) as this was by way of comparison with standards under vigorously controlled conditions and agrees with the reported work on the pyrolysis of organophosphorus compounds. Approximately equal confidence can be placed in those assignments resulting from close agreement of fragment and standard retention indices. For those cases where more than one fragment is noted or those involving compounds for which no standard index was determined (Table 13), the assignments were made on the basis of general observations of the relative retentions of the hydrocarbons under several different conditions (such as their sub-ambient temperature chromatography, next section) and must therefore be considered "probable" assignments.

The characteristic fragmentation product for MEHDPO was found to be 2-ethylhexene-1. It is not included in Table 16 because its excessive retention makes it a poor standard for the computation of other retention indices and its own retention index is known only approximately (Table 15, I = 664). A peak in the MEHDPO pattern appearing in the same position as the characteristic peak of n-hexyl diphosphine oxides was assumed to be hexene-1 and assigned a retention index of 592.

The agreement, using the assumed value, of the lower retention index values of MEHDPO with those of the other diphosphine oxides supports the assignment of hexene-1 to this peak.

An examination of Table 16 shows that each diphosphine oxide degrades with the formation of the 1-olefin characteristic of its alkyl side chain. For the diphosphine oxides containing the n-hexyl group (MHDPO, EHDPO, PHDPO, and BHDPO), the characteristic product is hexene-1. MNDPO, containing the neohexyl group, forms 3,3-dimethylbutene-1. MEBDPO, containing the 2-ethylbutyl group, forms 2-ethylbutene-1 on fragmentation. As mentioned above, MEHDPO (containing the 2-ethylhexyl group) yields 2-ethylhexene-1.

Most of the remaining fragmentation products in each pattern can be considered as resulting from the further breakdown of the respective 1-olefins. This is especially so for the four-carbon and smaller fragments. Some products, such as 2,3-dimethylbutene-2 and hexene-2, might arise from the thermal isomerization of the respective 1-olefins (3,3-dimethylbutene-1 and hexene-1 for the above products).

Very few products other than the characteristic 1-olefins can be visualized as being formed from primary breakdown processes. Pentene-1 might arise from primary breakdown of the n-hexyl diphosphine oxides by abstraction of a γ- rather than β-hydrogen (leaving a methyl group rather than a hydrogen atom bonded to phosphorus).

C_1-C_4 fragments

The programmed temperature study suggests the formation of secondary and tertiary phosphine oxides by cleavage of the methylene bridge. Examination of the C_1-C_6 fragment region supports the contention that secondary phosphine oxides could form. It was of interest to learn whether both phosphorus-carbon bonds of the methylene bridge were cleaved.

To test this possibility, the standards of Table 17 were chromatographed at 0°C and used to construct a standard chromatogram (Figure 28). The diphosphine oxides EHDPO, PHDPO, and BHDPO were fragmented and the fragmentation patterns (Figure 29) compared to the standard chromatogram. If such a cleavage occurs, an enhanced amount of butadiene-1,3 would be expected from BHDPO. Similarly, PHDPO and EHDPO would be expected to yield enhanced amounts of allene and acetylene respectively.

A study of Figures 28 and 29 and Table 17 shows that peaks are present which can be assigned to acetylene, allene, and butadiene-1,3. The relative amounts of these products formed is seen to be independent of the diphosphine oxide fragmented. Because some formation of these products is expected as a result of secondary breakdown of the characteristic 1-olefin, it can be concluded that "bridge release" does not occur to any appreciable extent. A comparison of the fragmentation patterns from MNDPO and MNDPO-U (Figure 30) shows that no significant effect on the C_1-C_4 region of fragments can be attributed to complexation.

Table 17. Peak assignments for the standard chromatogram of C_1-C_4 hydrocarbons

Number[a]	Standard	Number[a]	Standard
1	Methane	8	n-Butane
2	Acetylene	9	Butadiene-1,3
3	Ethane	10	Neopentane
4	Propane	11	trans-Butene-2
5	Allene	12	cis-Butene-2
6	Isobutane	13	3-Methylbutene-1
7	Isobutene		

[a]Number of peak in Figure 28.

Effect of Operating Parameters

Discharge severity

The influence of discharge severity (percentage of the maximum voltage setting multiplied by the resulting current in milliamperes) on the total area of the pattern* for MNDPO and MNDPO-U is demonstrated in Figure 31. It can be seen that discharge severity influences the total weight of products formed and does so equivalently for both the metal-ligand complex and the ligand. The fact that approximately the same area is obtained for the complex as for the ligand at any given discharge severity suggests that the chosen sample sizes, 0.10 mg. for the ligand and 0.15 mg. for the complex, present approximately equivalent amounts of breakable organic material for analysis. It is also apparent that maximum

*All work discussed in this and the following chapter involved the ambient column temperature patterns.

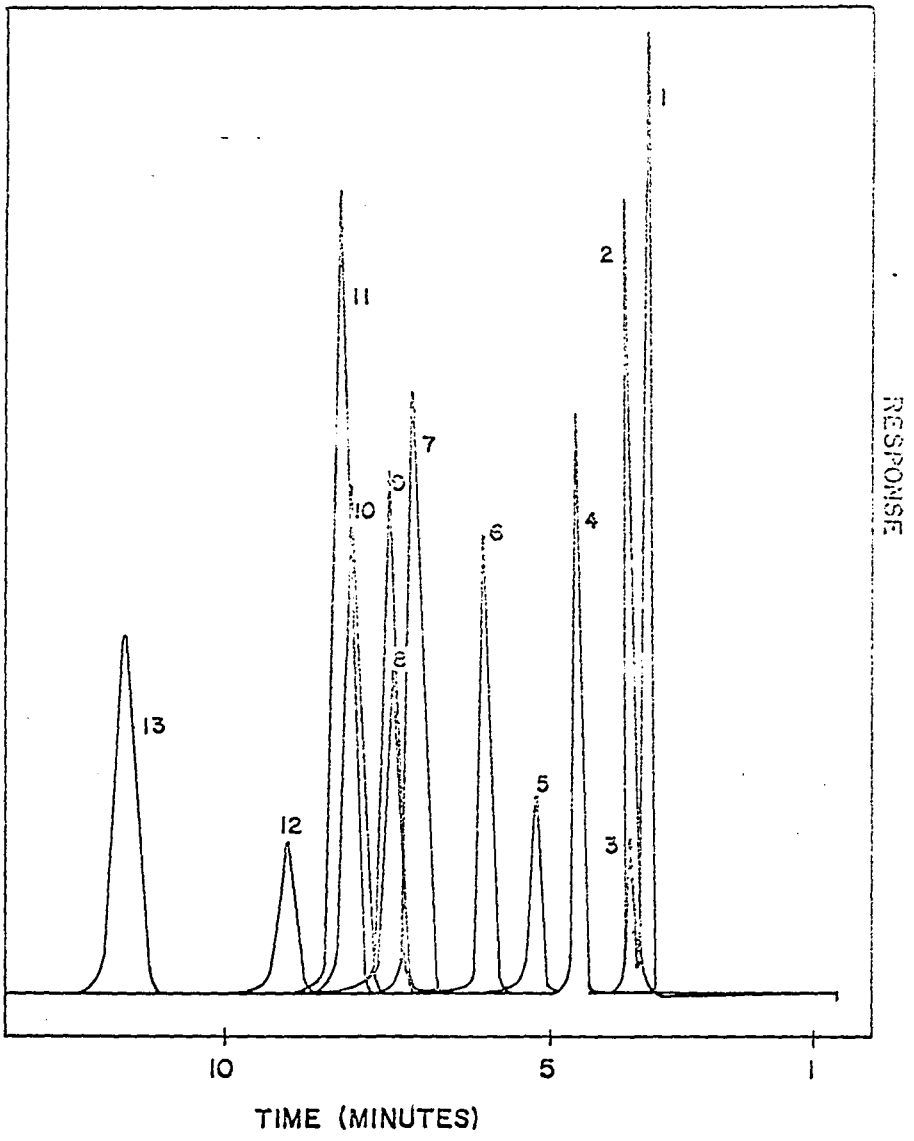


Figure 28. Sub-ambient column temperature standard chromatogram of C_1-C_4 hydrocarbons

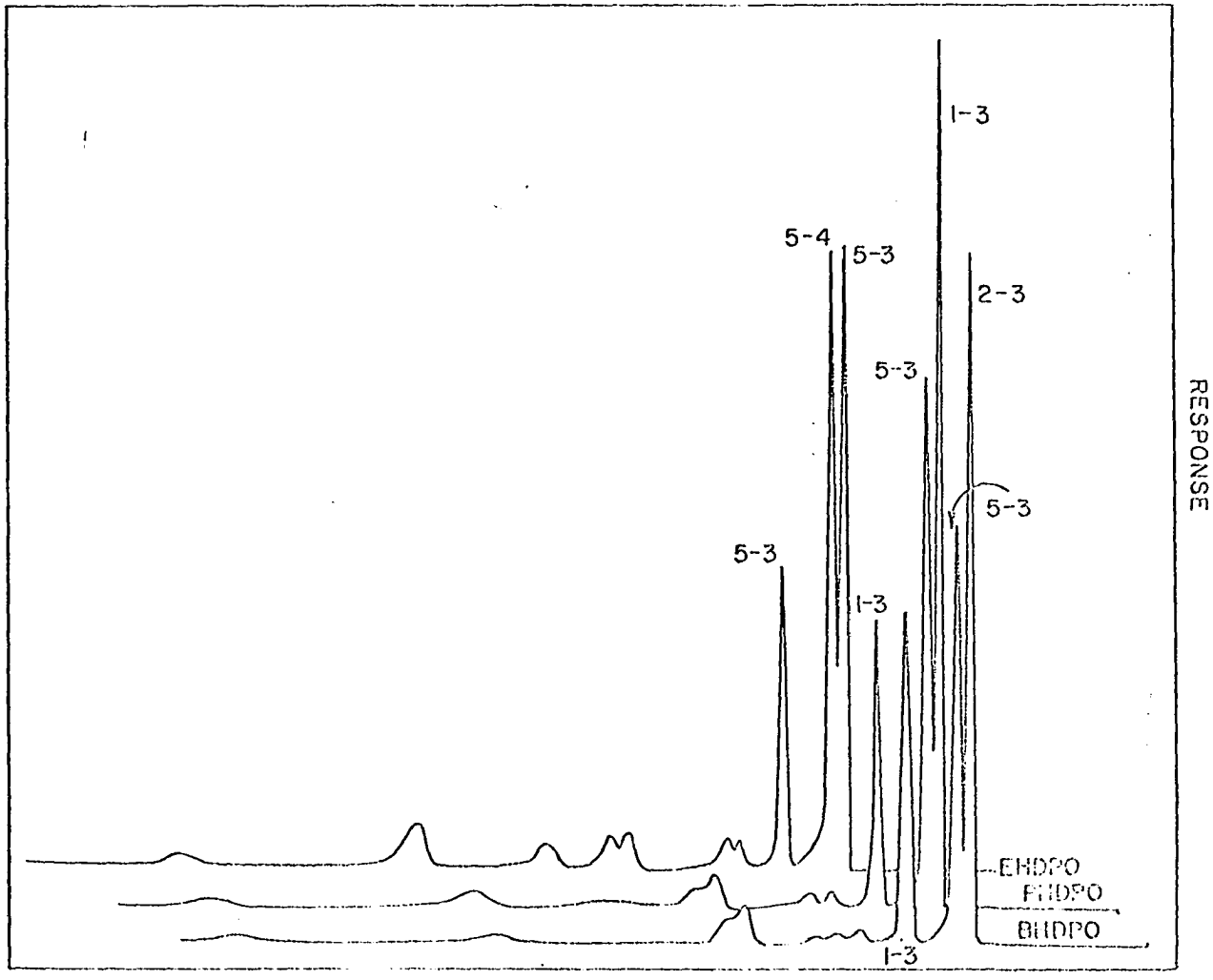


Figure 29. Sub-ambient colum temperature fragmentation patterns for EHDPO

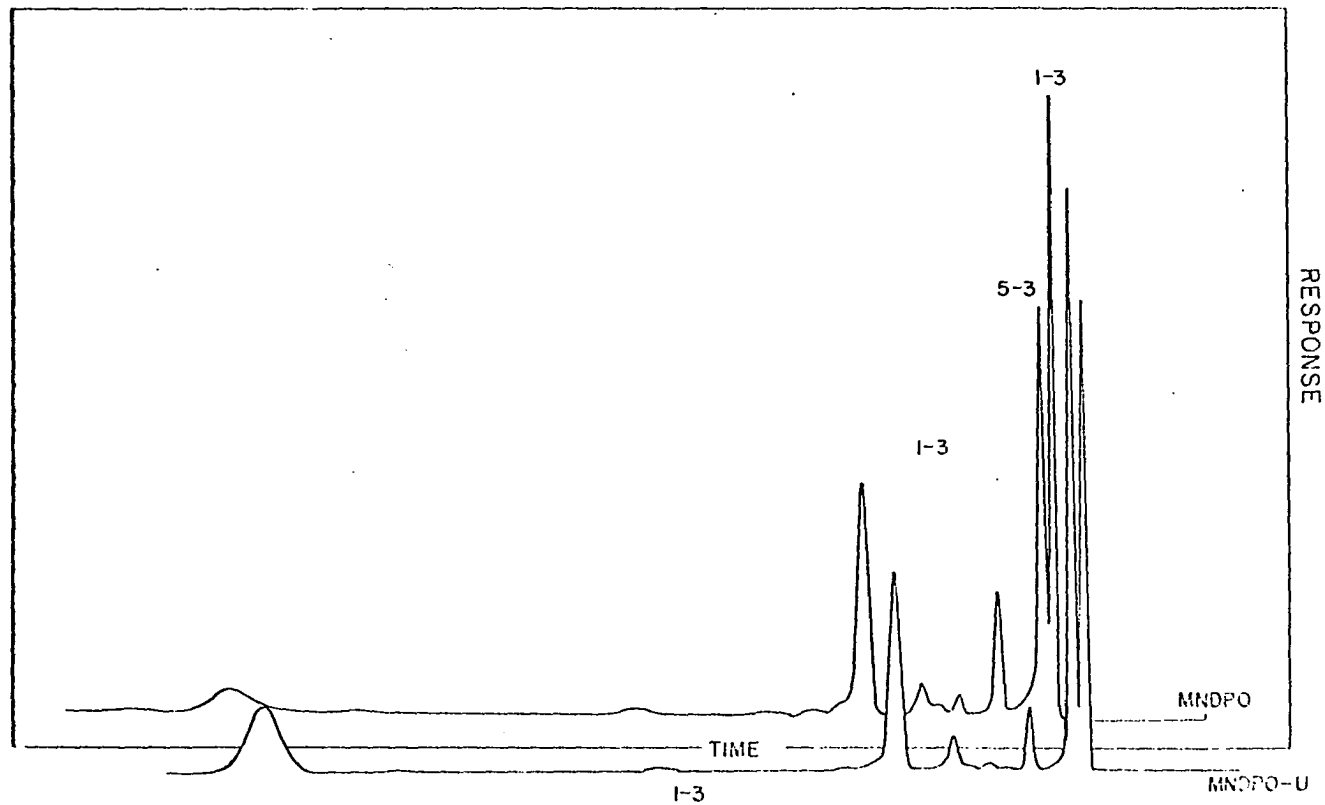


Figure 30. Sub-ambient column temperature fragmentation patterns for MNDPO and MNDPO-U

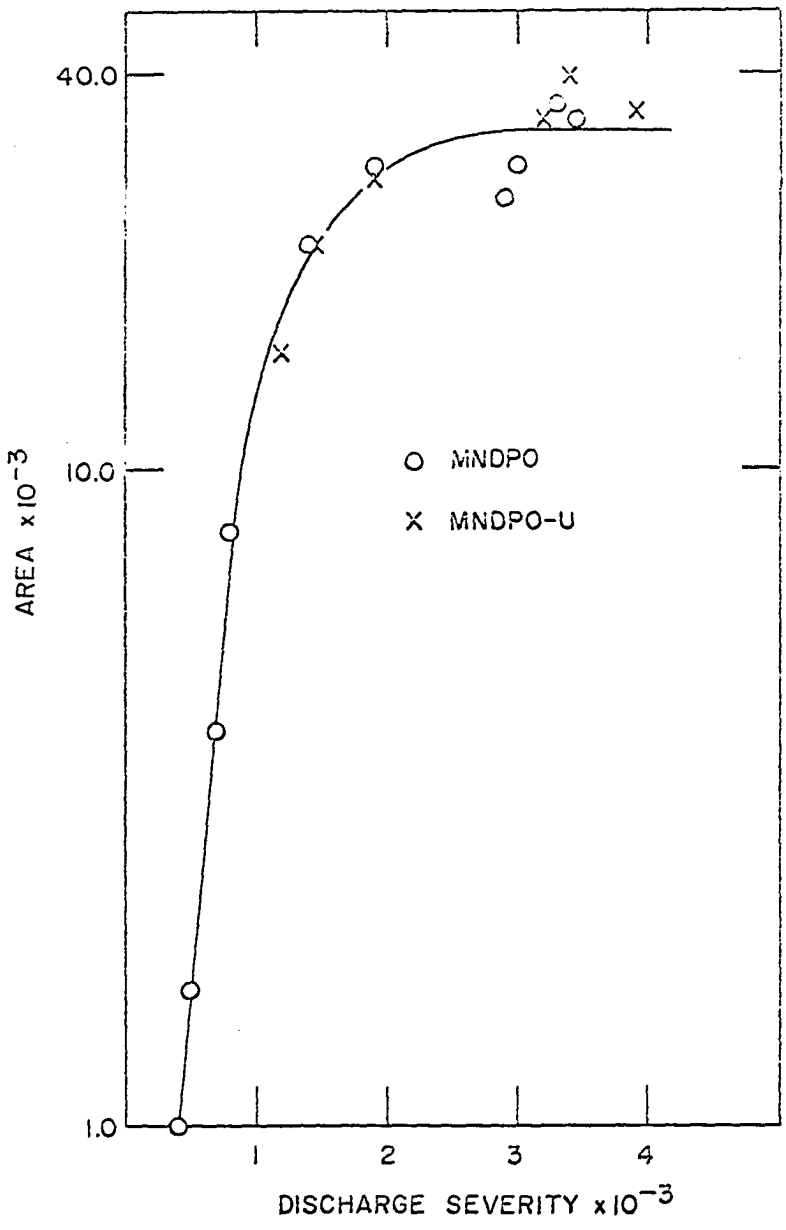


Figure 31. Variation in the area of the ambient column temperature fragmentation pattern for MNDPO and MNDPO-U with increasing discharge severity

degradation may be obtained within the accessible range of discharge severities (voltage = 40% of the maximum of 3500 volts resulting in a current of approximately 90 ma. for a discharge severity of 3600) when the given weights of samples are fragmented.

These data also allow the selection of a discharge severity yielding a balance between significant pattern size and maximum secondary breakdown (as would be expected (101, 102) for maximum severities). A discharge severity of approximately 1800 (voltage = 30%, current = 60 ma.) was chosen for those studies requiring constant discharge severity.

The influence of discharge severity on the peak height-average relative abundance of characteristic peak from MNDPO and MNDPO-U fragmentations is presented in Figure 32. It is seen that, as noted earlier, the peak height-ARA is consistently larger for the metal-ligand complex than for the ligand. It is also noted that the ARA for the ligand shows a slight decrease on increasing discharge severity and the ARA for the metal-ligand complex increases with increasing discharge severity.

The larger ARA* for the metal-ligand complex and opposite dependence of the ARA on discharge severity for the ligand and for the metal-ligand complex cannot be simply interpreted.

*ARA stated from this point on is read "average relative abundance" and always corresponds to the peak height-average relative abundance (including the methane-ethane region) of the characteristic 1-olefin in the ambient column temperature fragmentation pattern of the given compound.

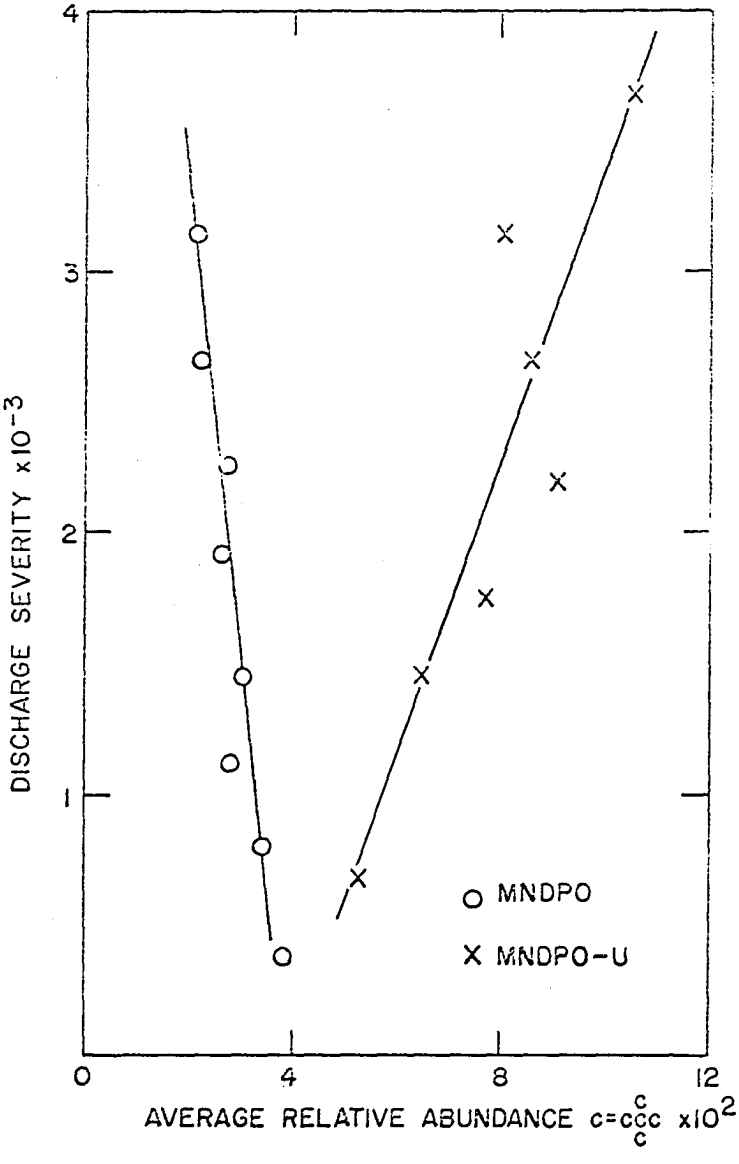


Figure 32. Variation in the peak height-average relative abundance of 3,3-dimethylbutene-1 from MNDPO and MNDPO-U with increasing discharge severity at constant discharge time (30 seconds)

Recalling the work (5) suggesting the involvement of the phosphoryl oxygens in a cyclic mechanism for the formation of the 1-olefins, it might be predicted that complexation should result in a smaller ARA because the phosphoryl oxygens, involved in complexation, would be less apt to readily abstract a beta-hydrogen from the alkyl side chains.

The slight decrease in ARA for the ligand on increasing the discharge severity could be interpreted as due simply to enhanced secondary breakdown under the more vigorous discharge conditions. The opposite behavior for complex is not as readily explained. In view of the reproducibility problem and the relatively small dependence of ARA on the discharge severity, additional evidence that the observed behavior is "real" is desirable (although the same behavior was noted three times on reproducing the experiment).

A similar study was carried out using EHDPO and EHDPO-U and, as can be seen from Figure 33, the same behavior was observed. Spot checks of the ARA values for MHDPO, MHDPO-U and PHDPO, PHDPO-U indicated similar behavior. In view of this consistency, the opposite dependence of ARA on discharge severity for complexed and uncomplexed ligand must be considered "real".

A possible interpretation of the dependence of ARA on discharge severity is presented in the next chapter. The important result of these data in evaluating the potential of the technique as an inorganic analytical tool is that an

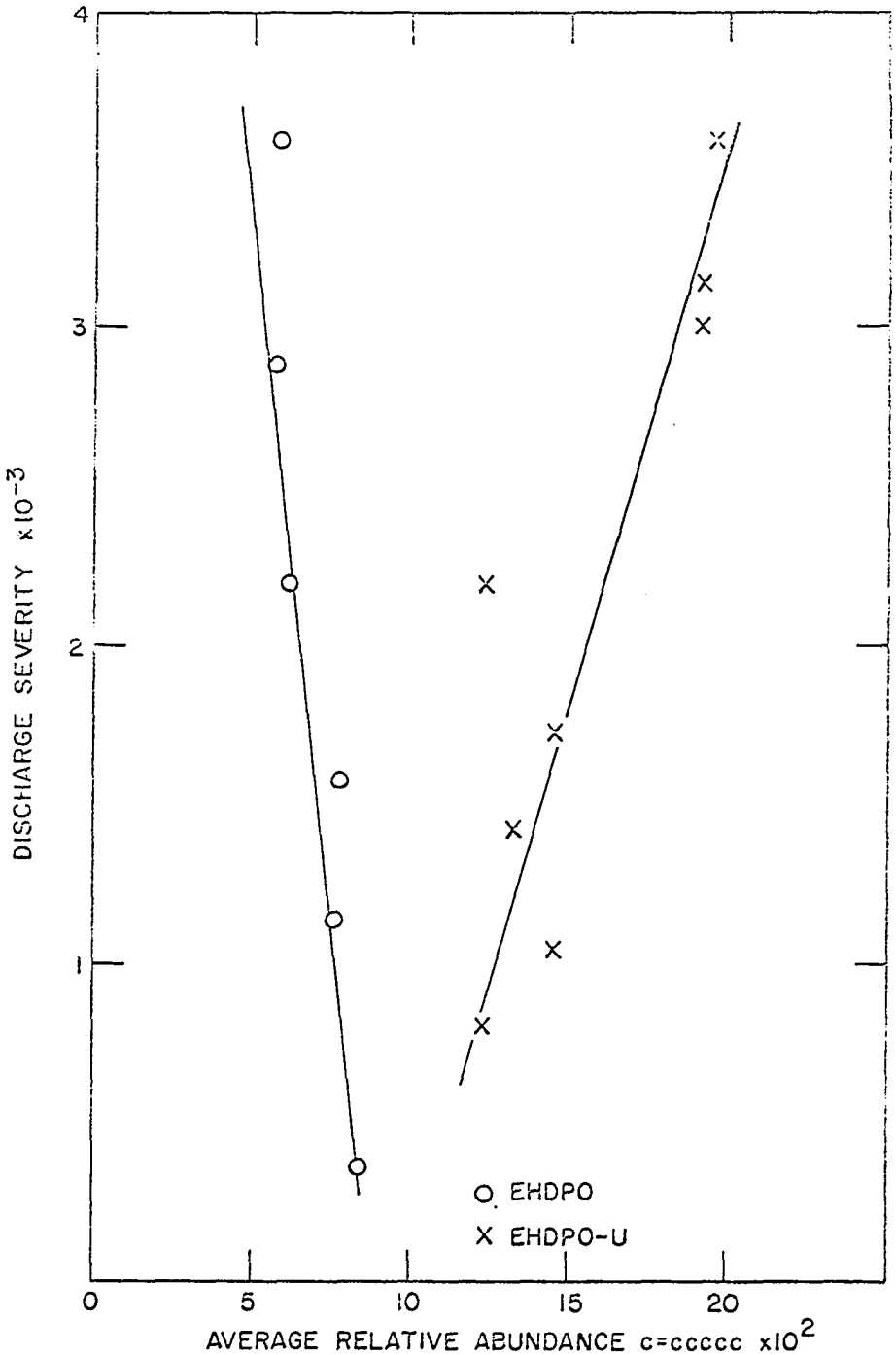


Figure 33. Variation in the peak height-average relative abundance of hexene-1 from EHDPO and EHDPO-U with increasing discharge severity at constant discharge time (30 seconds)

increase in discharge severity increases the difference between the ARA for the ligand and the ARA for the metal-ligand complex.

Discharge time

Figure 34 illustrates the influence of discharge time on the total amount of breakdown for MNDPO at three discharge severities. It is seen that maximum breakdown is approached more quickly at higher severities. At discharge severities of approximately 3600 and 1800, the maximum amount of breakdown is limited by the discharge severity whereas at 800, it is limited by the discharge time. Calibration of the peak areas shows that 100 µg. samples of MNDPO yield approximately 3 µg. of hydrocarbon at a discharge severity of 1800 operating for thirty seconds.

The influence of discharge time on the total pattern size is seen to be essentially the same for complexed and uncomplexed ligand (Figure 35). Plots of ARA as a function of discharge time for MNDPO and MNDPO-U have been found to be very similar to discharge severity plots. A slight decrease in ARA is noted for ligand and the opposite for the metal-ligand complex as discharge time is increased.

The effect of discharge time on the extent of fragmentation is as would be expected. The effect on ARA is not easily explained but might be reasonable because whatever effect results in a greater ARA for the complex than for the ligand

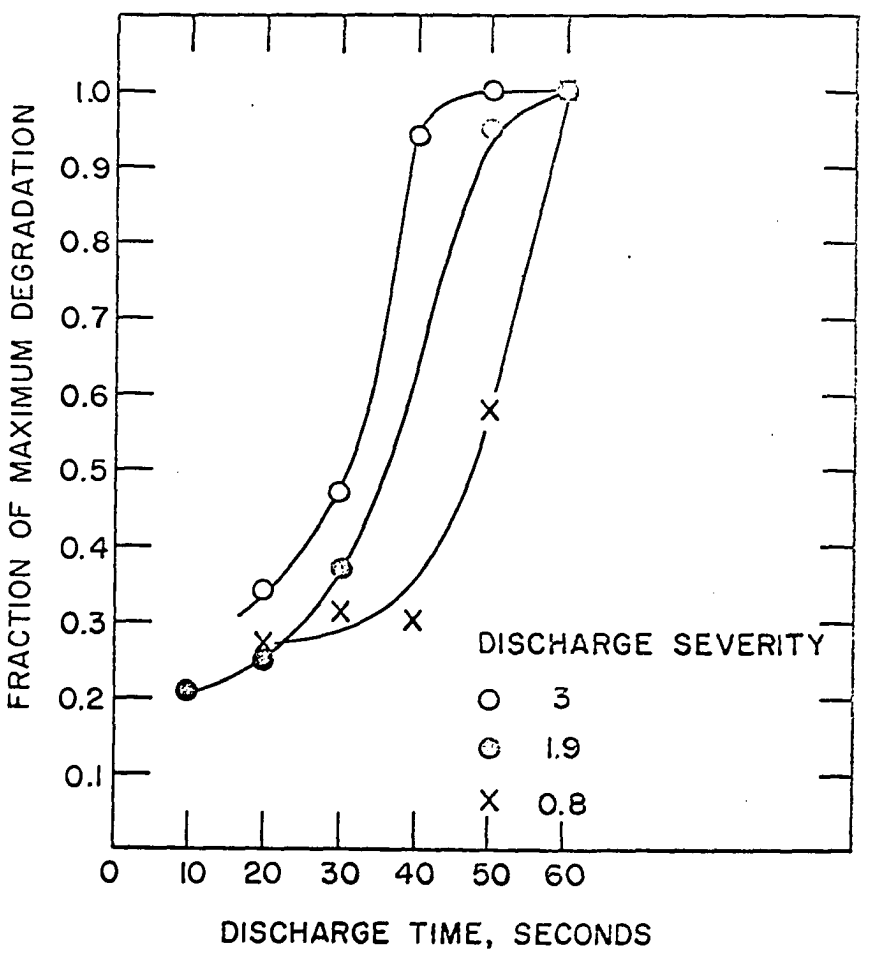


Figure 34. Variation in the extent of degradation of MNDPO with increasing discharge time at constant discharge severities ($x10^{-3}$) for 0.10 mg. samples

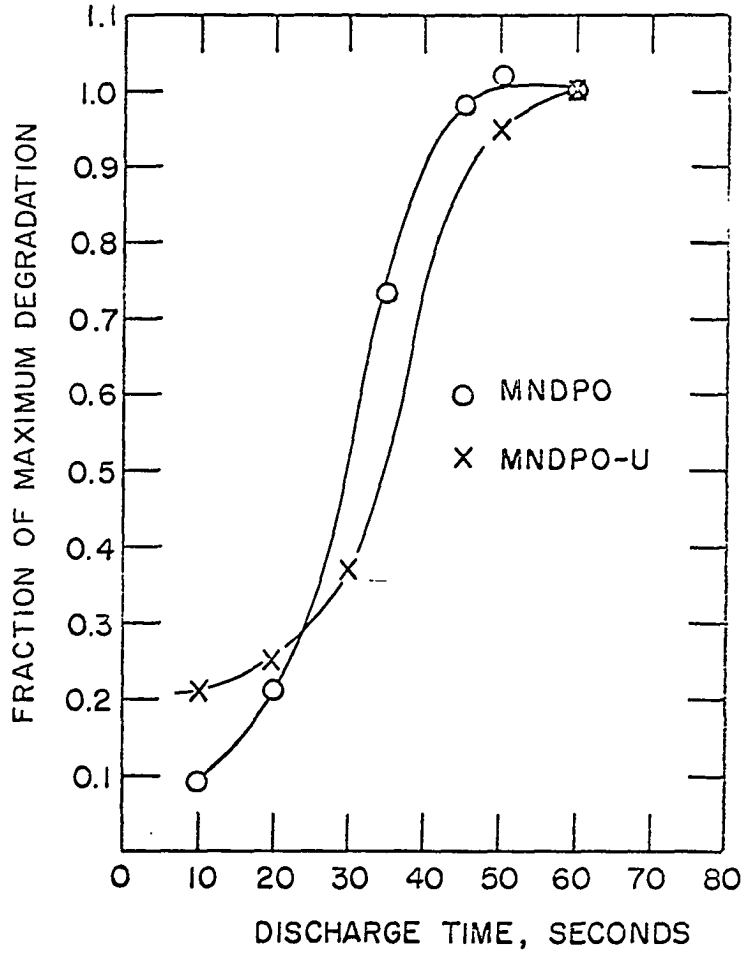


Figure 35. Variation in the extent of degradation of MNDPO and MNDPO-U with increasing discharge time at constant discharge severity for 0.10 and 0.15 mg. samples respectively

at a given discharge time might be expected to result in a greater difference if allowed to operate for a longer time.

Flow rate

The influence of purge-line carrier gas flow rate on the ARA was briefly investigated. Figure 36 demonstrates this influence for MNDPO.

The increasing ARA with increasing flow rate can be explained simply on the basis of a decreased probability of secondary breakdown at higher flow rates. The faster the flow, the more rapidly the primary breakdown products can leave the discharge zone.

It is seen that slight fluctuations in flow rate do not result in significant changes in ARA. Because flow rate does exert a measurable effect on ARA, data that are to be compared must be obtained at approximately equal flow rates.

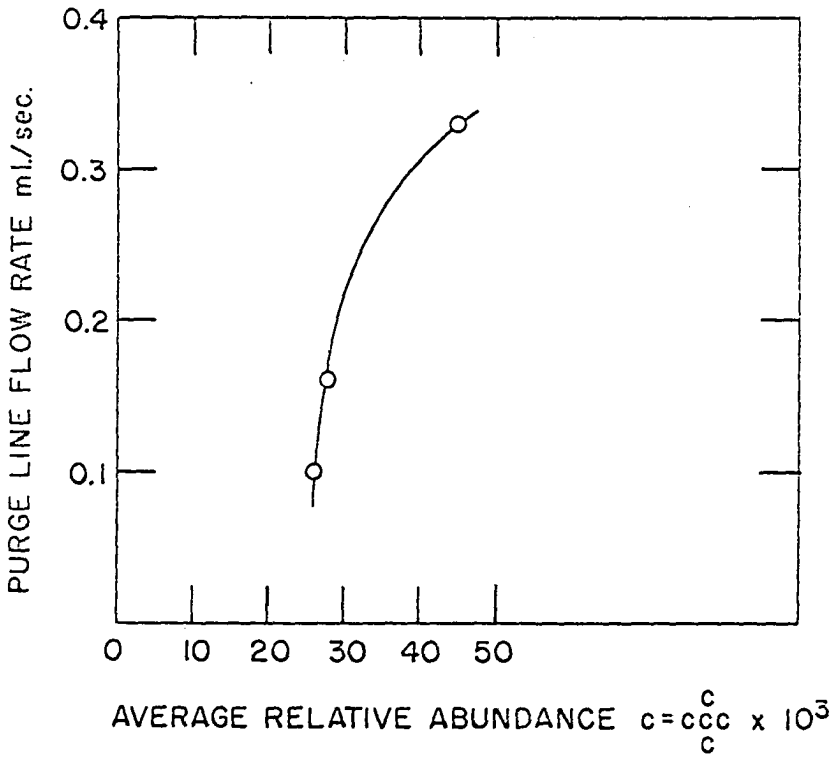


Figure 36. Variation in the peak height-average relative abundance of 3,3-dimethylbutene-1 from MNDPO with increasing purge line flow rate

INTERPRETATION OF RESULTS

Enhanced Secondary Breakdown

Enhanced secondary breakdown was studied by comparing fragmentation patterns of MNDPO obtained with the sample placed in its normal downstream position with those obtained with the sample placed near the upstream electrode. If the mechanism of fragmentation involves breakdown of the solid sample and the subsequent volatilization of the fragments (primarily 3,3-dimethylbutene-1 for MNDPO), it would be expected that placement of the sample nearer the upstream electrode would result in a lower ARA because the volatilized fragments would have a greater chance of undergoing secondary breakdown than if they were formed nearer the downstream (exit) electrode.

When fragmentation patterns were compared, it was found that the ARA was actually three times as large under enhanced secondary breakdown conditions as under normal operating conditions. It was also noted that the total pattern size was consistently smaller when the sample was positioned nearer the upstream electrode.

These findings suggest the possibility of vapor phase fragmentation of volatilized diphosphine oxide rather than fragmentation of the solid. Assuming that the proximity of the solid sample to the exit of sample tube and the direction of flow of the carrier gas restricts the volume occupied by

the diphosphine oxide vaporized at the downstream electrode while allowing that formed at the upstream electrode to occupy the entire volume of the tube, allows interpretation of the observed pattern sizes and the average relative abundances. The result of the stated assumption is that the sample originating at the upstream electrode would be present in a smaller vapor phase concentration than that originating at the downstream electrode. It is known that smaller vapor phase concentrations result in a smaller percentage degradation (101), therefore, a smaller amount of 3,3-dimethylbutene-1 and a smaller total pattern size would be expected to be produced by the MNDPO originating at the upstream electrode. Because a smaller concentration of the olefin results in a smaller chance of further breakdown (6,61,101), a larger ARA would be expected.

A similar argument can be applied to the mechanism for the fragmentation of the solid to show that ARA actually could be larger under the conditions for enhanced secondary breakdown than "normal" operating conditions. However, total pattern size would be expected to be independent of sample placement for the fragmentation of the solid because the same amount of 3,3-dimethylbutene-1 is assumed to form in either case.

Other evidence exists which supports the contention that MNDPO is volatilized intact during discharge. The most

significant evidence is the detection (by gas chromatography) of undegraded diphosphine oxide on the inner surface of the downstream electrode after a sample is fragmented.

Direct-to-Detector Studies

If the effluent of the fragmentation tube is piped directly to the detector, the recorder trace obtained is a plot of the weight (indirectly) of products formed as a function of discharge time. The area of the trace is a measure of the total weight of products formed under the given conditions.

Typical traces for the fragmentation of MNDPO and MNDPO-U are presented in Figure 37. Whereas actual shapes of the traces vary somewhat from run to run, it is always noted that the response for MNDPO-U is considerably more ragged than that for MNDPO. This indicates that the fragments from the complexed ligand are formed in pulses as opposed to a more regular formation from uncomplexed ligand.

A regular versus pulse formation of products can be interpreted assuming a vapor phase fragmentation mechanism. For ligand, the sample can simply vaporize into the discharge and undergo fragmentation with a resulting "regular" formation of product. For complexed ligand, the process is more complicated. The sample cannot vaporize into the discharge without a prior rupture of metal-ligand bonds. A mild fragmentation process must occur before the diphosphine oxide is free to vaporize.

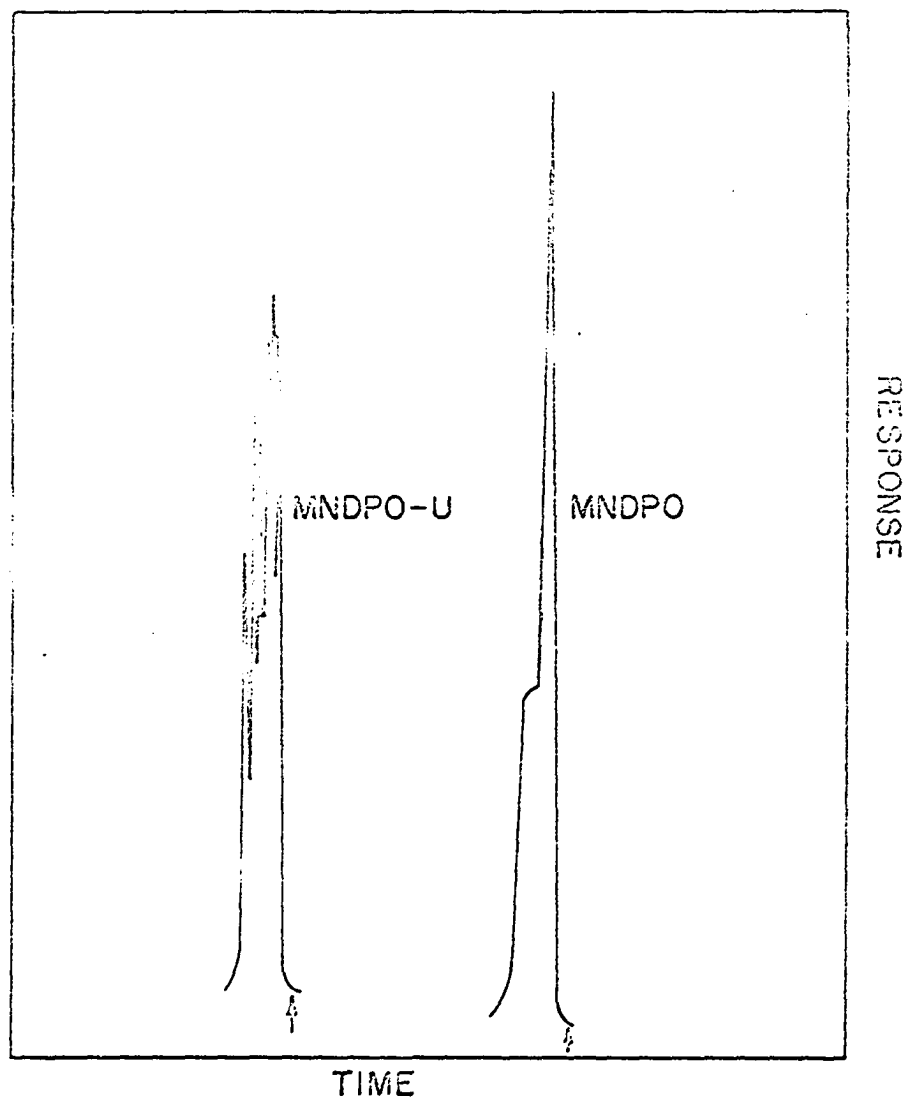


Figure 37. Direct-to-detector traces for MNDPO and MNDPO-U

A basic difference between vaporization and pyrolysis is that vaporization is a surface phenomenon whereas pyrolysis is an internal phenomenon (69). In fragmentation (pyrolysis), products are formed within the sample and then escape (69). It might be expected that this "formation-and-escape" mechanism would result in a much less regular evolution of products than would result from a surface mechanism.

The difference in the way the products are formed from MNDPO and MNDPO-U can, then, be the result of a difference in effective-sampling. A regular vaporization of MNDPO might yield a regular formation of products. A release of MNDPO in pulses might yield a pulse-like formation of fragments.

In the course of several investigations, it was noted that increasing discharge severity had different effects on the "raggedness" of the direct-to-detector traces for ligand than for the complex. Although no good "raggedness" parameter could be found to characterize the discontinuity in the various patterns, a general measure of the effect can be obtained by plotting discharge severity as a function of the number of "peaks" (pulses) in each trace. This is shown, with a value of "1"being assigned for each peak and "0.5" for each shoulder, in Figure 38. It can be seen that increasing severity increases the discontinuity of the trace for the metal-ligand complex but has little-to-no effect on the trace for the ligand. It is possible to visualize the different operating

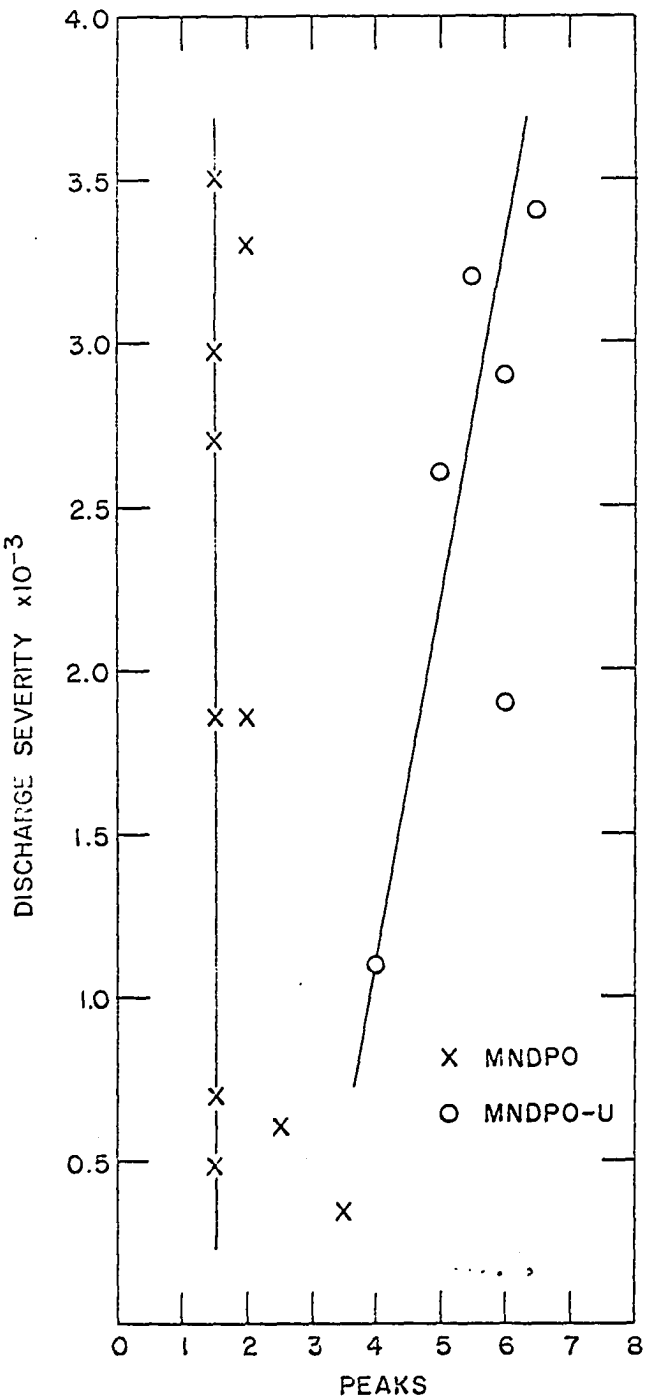


Figure 38. Variation in the number of peaks in direct-to-detector traces for MNDPO and MNDPO-U with increasing discharge severity

parameter dependence of complex and ligand and the larger ARA for complex than ligand by simply considering the probability of secondary breakdown if this effective-sampling difference is evoked as the cause.

Consider two fragmentations such that the total amount of sample introduced into the breakdown region is the same for both but in one case the vaporization of sample is regular while in the other it occurs as small pulses. Ideally, a plot of the amount of sample vaporized as a function of discharge time (indirectly, a direct-to-detector trace) for regular vaporization (I) would look like a normal distribution curve and for pulse vaporization (II) like a series of sharp, partially overlapping peaks. Because the same total amount is vaporized, the area of I equals the area of II. Assuming that sufficient time exists for a given pulse of sample to occupy the entire fragmentation tube prior to significant breakdown and that the breakdown products and unbroken sample of a given pulse leave the fragmentation tube before the next pulse refills the tube, it is possible to visualize the influence pulse sampling may have on ARA.

Because the total areas of above described traces are equal (assumed above and essentially the situation experimentally in comparing MNDPO and MNDPO-U fragmentation) the areas (weights of sample) of each pulse are a small fraction of the total area. If this amount occupies the fragmentation

tube, the result is a much smaller concentration of sample which results in a smaller percentage breakdown (101) and lessened secondary breakdown conditions with a subsequent increase in ARA. The total fragmentation pattern can be visualized as the result of the summation of these individual breakdowns.

Although this allows visualization of the process, it does not offer a valid explanation because it necessarily assumes that the "pulse" of sample occupies the volume of the discharge tube for the same length of time as does the entire vaporized sample from uncomplex ligand. The fragmentation process is much more complicated than a simple release of discrete, equal sized pulses of sample. Obviously, the pulses overlap and are not equal in size.

If the percentage breakdown and subsequent probability of secondary breakdown were directly proportional to concentration, the ARA resulting from the series of pulses would equal that resulting from the more regular vaporization of sample because, having the same total area, the same amount of sample is released into the discharge. However, for electrical discharge pyrolysis, it has been shown (101) that the dependence of percentage breakdown on vapor phase concentration is not strictly linear but falls off at lower concentrations. As a result, the difference between the ARA from an average sized pulse and that for a very small pulse is greater than that

between an average and larger sized pulse. The net result is an increased ARA for pulse sampling.

On increasing discharge severity, both the number of pulses and total area of the direct-to-detector traces for MNDPO-U increase. It has been found, however, that the increase in severity increases the discontinuity somewhat more than it does the total area. As a result, the average area per pulse decreases (more small pulses) thus increasing the ARA. Since "area per pulse" reflects the sizes of the pulses, this parameter would be expected to better describe ARA effects for the fragmentation of the complexed ligand than would the total area of the pattern.

Discussion

The effective-sampling concept predicts a significantly different total pattern size dependence of ARA for complexed ligand than for uncomplexed ligand. For uncomplexed ligand, an increased pattern size would be expected to result in a decreased ARA since the probability of secondary breakdown increases with increasing sample size (6,61,101). Pattern size per pulse is postulated as the more important factor for determining the ARA from the complex. Plots of total pattern size (as determined at different discharge severities) as a function of ARA for MNDPO and MNDPO-U show a steady decrease in ARA with increasing pattern size for MNDPO and no dependence of ARA for MNDPO-U. Significantly, plots of total

pattern size at constant discharge severity as a function of ARA for ligand show a pattern size dependence (Figure 39). No correlation between total pattern size and ARA from complexed ligand has been noted. A plot of total pattern size per pulse versus ARA for NNDPO-U (Figure 40) shows a general decrease in ARA with increasing average pulse size.

It must be pointed out that any conclusions based on data involving "raggedness" can only be indicative since no accurate measure of the number of pulses is possible. The strength of the argument that complexation effects are the result of pulse sampling and subsequent vapor phase fragmentation lies in the large number of observations interpretable by the concept. It has been shown that the larger ARA from the metal-ligand complex than from the ligand and the discharge severity dependence of ARA can be rationalized using this concept. The difficulties encountered in obtaining reproducible values for the ARA and total pattern sizes might be expected to be associated with the difficulty of reproducing the sampling step of the vapor phase degradation process. The ability to obtain larger pattern sizes with smaller sample sizes can be understood since the size of the pattern is dependent on the volatilization process and not necessarily the amount of solid sample loaded. The small percentage fragmentation can be understood as due to the escape of a large fraction of the sample via volatilization. Since the

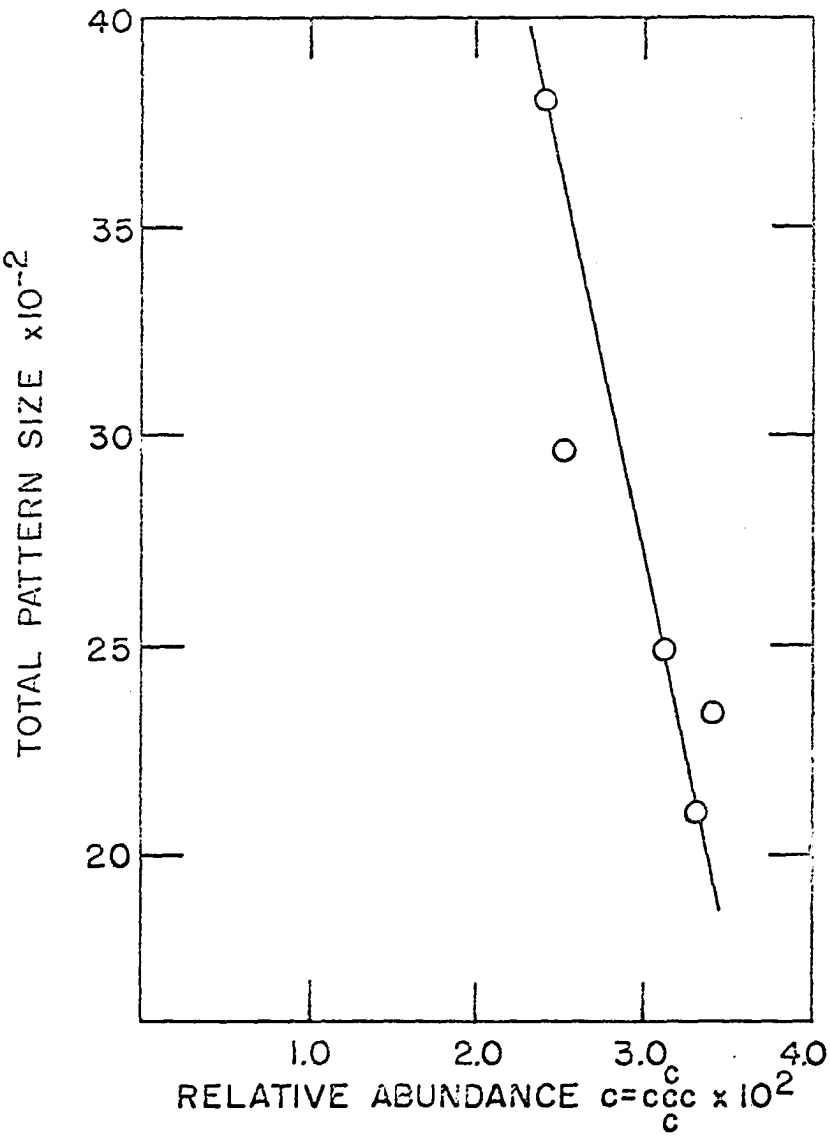


Figure 39. Variation in the peak height-relative abundance of 3,3-dimethylbutene-1 from MNDPO with increasing total size of the fragmentation pattern

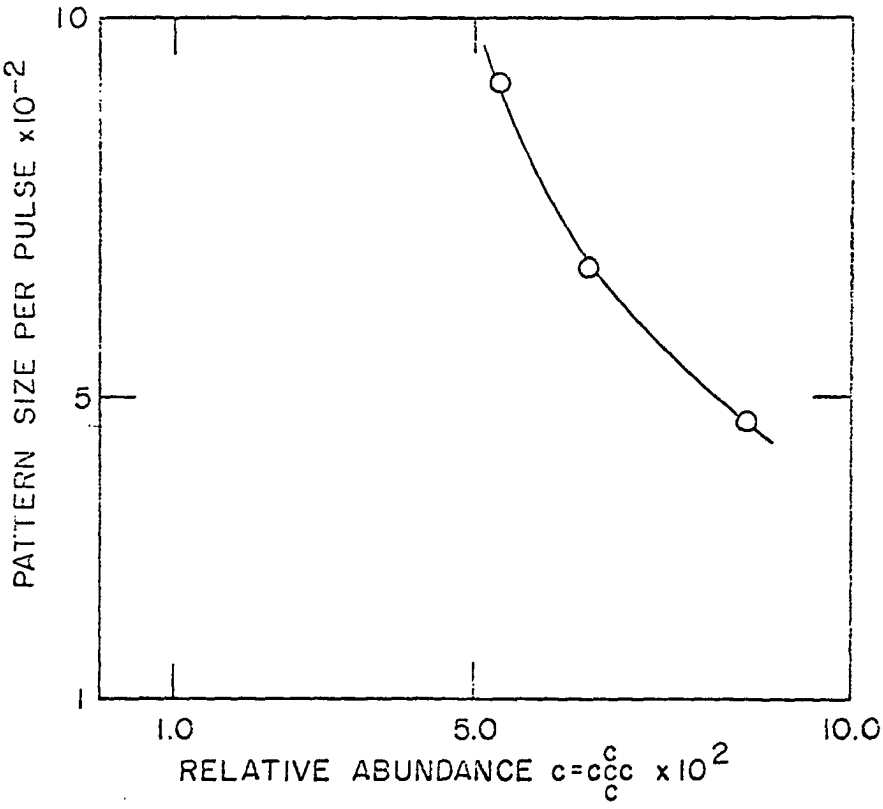


Figure 40. Variation in the peak height-relative abundance of 3,3-dimethylbutene-1 from MNDPO-U with increasing total pattern size per pulse

total amount of sample per pulse can change as a function of time, discharge time could influence ARA. The concept of the pre-vaporization of sample can also account for the differences in ARA values and standard deviations observed as a function of the sampling procedure (Table 12).

QUANTITATIVE ANALYSIS

The difficulty encountered of obtaining quantitatively reproducible breakdown patterns mitigates against applying fragmentation-gas chromatography to quantitative analytical problems. It is a great temptation to ascribe this reproducibility problem to the electrical discharge fragmentation unit. This is especially so in view of claims (59) that fragmentation patterns resulting from other types of units can be as reproducible as mass spectra and quoted (6) breakdown reproducibilities of 0.5 per cent for filament fragmentation. The chances are much greater, however, that the poor pattern reproducibility is a function of the attempted application.

The necessity of working with low-boiling fragments results in the use of fragmentation patterns containing strong if not major contributions from secondary breakdown. This would be expected to greatly decrease pattern reproducibility. Equally important, the samples fragmented are of significant volatility. The pre-fragmentation volatilization of sample or volatilization during fragmentation (as postulated for the diphosphine oxides) would be expected to severely diminish quantitative pattern reproducibility because such a volatilization would be expected to be poorly reproducible.

A means does exist to lessen the reproducibility problem. If the sample to be analyzed is spiked with a known amount of a similar compound (a standard), it is possible to use the

ratio (size of characteristic peak from sample)/(size of characteristic peak from standard) as a measure of the amount of sample present. It has been found (Table 18) that this ratio is much more reproducible than absolute pattern sizes, peak sizes, and ARA values. Figure 41 demonstrates the potential of this approach for the analysis of the diphosphine oxides.

The fact that complexation does not direct the formation of products characteristic of the metal-ligand complex is at least as detrimental to the application of the fragmentation-gas chromatography of complexes to quantitative inorganic analysis as is the reproducibility problem. If fragmentation patterns from mixtures of complexed and uncomplexed ligand contained a peak or peaks characteristic of complexed ligand, an internal standard technique similar to that described for the diphosphine oxides might allow quantitative inorganic analysis. Without the presence of a peak from only the complexed ligand, the metal content of the fragmented sample must be related to a more minor complex-sensitive aspect of the fragmentation pattern.

An examination of Figure 42 shows that a relationship does exist between the ARA and amount of complexed ligand present in a mixture of metal-ligand complex and ligand. This curve was obtained under conditions approximating those of a practical analytical procedure. Known amounts of uranyl nitrate were added to solutions containing a given weight of

Table 18. Sensitivity of the internal standard ratio to operating conditions

Purge line		Discharge		Discharge		Sample	
Flow rate (ml./min.)	Ratio[a]	Time (sec.)	Ratio[a]	Voltage (%)[b]	Ratio[a]	Size (l)	Ratio[a]
24	0.70	5	0.64	20	0.82	1	0.68
15	0.67	10	0.62	25	0.71	2	0.68
12	0.67	15	0.72	30	0.67	3	0.72
10	0.70	20	0.78	35	0.68	5	0.68
5	0.76	25	0.76	38	0.70	10	0.68
4	0.67	35	0.78	40	0.71		

[a]Peak height ratio = 2-ethylhexene-1/2-ethylbutene-1.

[b]Percentage of maximum.

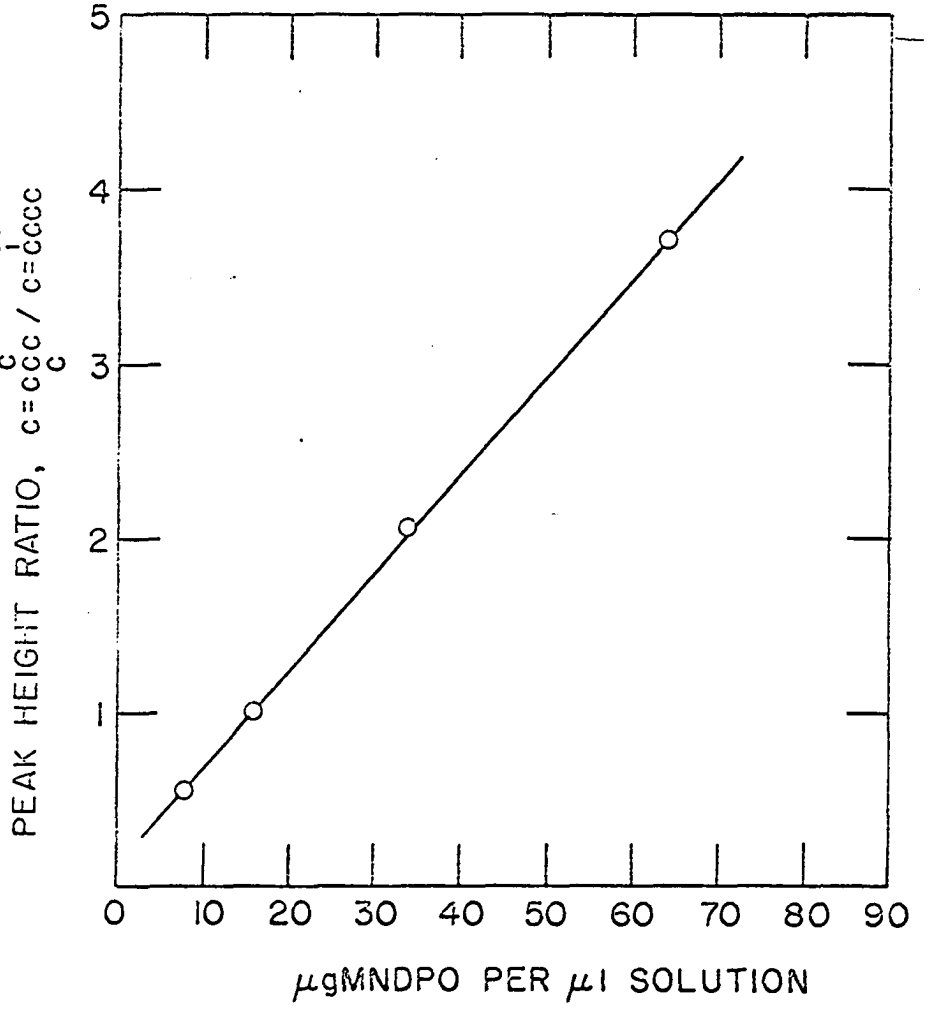


Figure 41. Calibration curve for the quantitative determination of MNDPO using MEBDPO as an internal standard

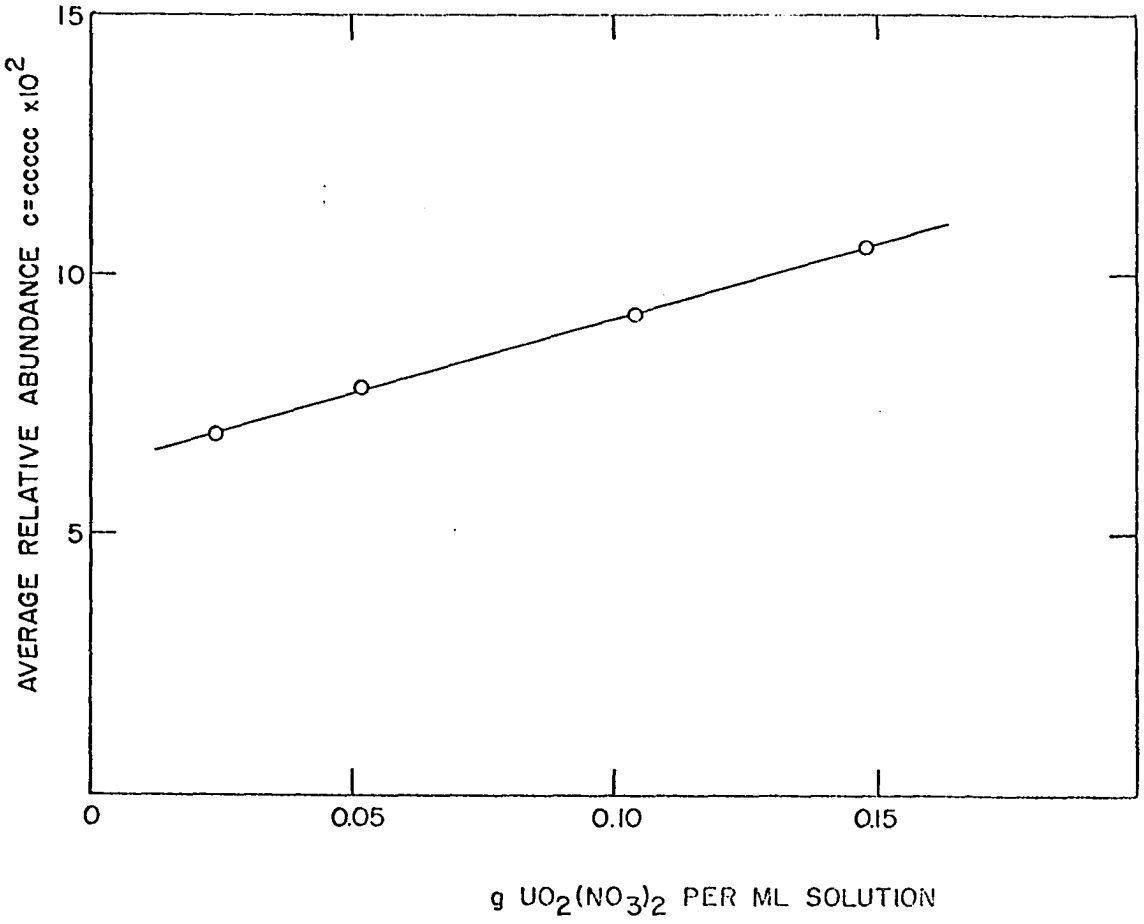


Figure 42. Variation in the peak height-average relative abundance of hexene-1 with increasing uranyl nitrate concentration in a solution of MHDPO and uranyl nitrate in 1,2-dichloroethane

MHDPO, a given volume of solution was deposited on the carbon-wool in a sample tube, the solvent evaporated in the valve compartment, and the residue was fragmented. This plot could be used as a calibration curve for the fragmentation-gas chromatographic analysis of uranium and as such demonstrates the possibility of inorganic analysis by this technique.

It also shows, however, that very little could be expected of such a technique. The small slope (Figure 42) indicates that sensitivity would be low. In view of the previous studies, selectivity would be expected to be virtually absent. The precision of the method would be very low. Recalling that calibration curves, such as that of Figure 42, can be obtained only with a large number of runs contributing to each point, the technique would be tedious.

In short, although it can be shown that fragmentation-gas chromatography is capable of being applied to quantitative inorganic analysis, the complications and limitations of the technique in its present form give it little practical value for such an application.

SUMMARY

Electrical discharge fragmentation-gas chromatography is applied to the diphosphine oxides and their solid uranyl nitrate complexes to evaluate the technique as a means of identifying the ligands and to find whether complexation influences the fragmentation in a manner allowing the quantitative analysis of the metal. The ability to reach definite conclusions is severely hampered by poor reproducibility of the quantitative aspects of the obtained fragmentation patterns.

Fragmentation patterns obtained by programming the column temperature are found sufficiently compound-specific to allow their use in identifying the diphosphine oxides. The positions of the peaks in the programmed column temperature fragmentation patterns suggest the rupture of the methylene bridge and the formation of phosphines and secondary and tertiary alkyl phosphine oxides as major degradation products. Complexation exerts no influence on the types of fragments formed but might influence the relative amounts of fragments formed.

Examination of the C_1-C_6 fragment region shows release of characteristic olefin from the alkyl side chain of the diphosphine oxide to be the primary fragmentation process contributing to the ambient column temperature fragmentation patterns. The alkyl substituent of a diphosphine oxide may be positively identified by monitoring the peak positions of the C_1-C_6 frag-

ments. Complexation is found to exert no influence on the types of products formed but does influence the relative amount of characteristic olefin formed. The average relative abundance (ARA) of characteristic product is consistently larger for complex than for ligand.

Close examination of the C_1-C_4 fragments suggests that no methylene bridge release occurs on fragmentation. Complexation exerts no effect on the C_1-C_4 fragment region.

Increasing discharge severity is found to result in decreasing the ARA of the characteristic olefin from ligand and to increase the ARA from the corresponding metal-ligand complex. Increased discharge severity increases the total amount of breakdown equivalently for complex and ligand.

Increasing discharge time also results in a slight decrease in ARA for the ligand and in increase for the complex. The influence of discharge time on total pattern size is dependent on the discharge severity, but is equivalent for complex and ligand. Maximum hydrocarbon formation is found to correspond to approximately five per cent of the total available hydrocarbon. Increasing purge line flow rate is found to result in an increasing relative amount of characteristic olefin in the patterns for MNDPO.

Evidence that diphosphine oxide volatilizes intact with subsequent vapor phase degradation and of a pulse-like formation of products from the metal-ligand complex versus a more

regular formation of products from the ligand suggests the complex sensitivity of ARA is the result of a difference in effective-sampling.

It is found possible to relate ARA to the metal content of the fragmented sample. The reproducibility problem and postulated basis of the complex-sensitivity of ARA suggest that little practical value can be assigned to the fragmentation-gas chromatography of metal-ligand complexes as an inorganic analytical tool. An internal standard technique is found to lessen the difficulties for the quantitative analysis of diphosphine oxides.

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APPENDIX

The retention index of a solute x, defined (54) as

$$I_x = 100 \frac{\log_{10} t_x - \log_{10} t_s}{\log_{10} t_{s'} - \log_{10} t_s} + 100z$$

where t_x is the adjusted retention time (distance) of the solute, t_s the adjusted retention time (distance) of an n-alkane of z carbons, and $t_{s'}$, the adjusted retention time (distance) of an n-alkane of z + 1 carbons such that

$$t_s \leq t_x \leq t_{s'} ,$$

is widely accepted (35) as the best manner of presenting retention data when peak identification is of interest.

To compute the retention index of a given sample, the sample is chromatographed along with n-alkanes differing by one carbon such that one alkane emerges just before the sample peak and the other emerges just after the sample. The adjusted retention times or distances are measured and the expression above is used to compute the retention index of the sample. A graphical method (50) of obtaining retention indices may also be used.

It would be best to use the same procedure for the computation of the retention indices of the peaks in fragmentation patterns. Generally, this is not possible since spiking the sample (with n-alkanes) to be fragmented complicates the fragmentation pattern. The simple expedient of pre-determining the adjusted retentions of n-alkanes may be employed but

results in less meaningful indices because it must be assumed that the values determined for the n-alkanes do not change as a function of time.

In the course of an investigation of structural retention parameters, the relation $\Delta R_m = b/100 \ (\delta I)$ where $\Delta R_m = \log_{10} t_2 - \log_{10} t_1$, $\delta I = I_2 - I_1$, (subscripts mean "compound" 1,2) and $b = \log_{10} t_{s+} - \log_{10} t_s$ (slope of retention vs. carbon number plot for n-alkanes), was derived using the gas chromatographic definition of R_m (63) and the definition of the retention index. Use of this relation allows the equating of many retention parameters (44). More important, it furnishes an additional means of computing retention indices for the peaks in fragmentation patterns.

All that is required to apply the ΔR_m expression to the computation of the retention indices of the peaks in fragmentation patterns is the determination of the retention index of one of the fragmentation products and the value of "b". Since "b" is characteristic of the particular column used and highly insensitive to most operating conditions (Table 19), it may be determined once and the value used with confidence for all subsequent computations (provided significantly different operating conditions such as different column temperatures, are not employed). An examination of Table 20 gives a measure of the agreement between the values of retention indices as computed using the definition of the retention index and those computed using the ΔR_m expression.

Table 19. Sensitivity of the constant "b" to operating conditions

Percentage liquid phase[a] (w/w)	"b"	Carrier gas flow (ml./min.)	"b"	Operating time[b] (hrs.)	"b"
6	0.313	48	0.318	27	0.317
12	0.316	67	0.319	32	0.316
18	0.318	79	0.317	46	0.317
27	0.319	97	0.319	55	0.318
		113	0.317	70	0.318

Table 20. Comparison of retention indices via Kovats definition and ΔR_m relation

Compound	Index via definition	Index via ΔR_m
n-Pentyl chloride	748.2	748.0
n-Heptyl chloride	950.3	949.6
Ethyl benzene	875.9	875.4
Toluene	767.2	767.6
n-Pentyl alcohol	712.3	712.5
Cyclohexanone	867.2	867.1

The use of retention indices to characterize fragmentation patterns has more than enough advantages to justify the extra effort in computation. In addition to being less dependent upon operating conditions, the values are descriptive in that they immediately classify the position of the peak with respect to the position of the n-alkanes. In certain cases, retention indices may be predicted from boiling points (35,64). The difference in retention indices of a given compound on two different columns (64) or of two compounds on a given column (35,57,104) can also be used to predict

the structure of the chromatographed compound.

For the fragmentation patterns presented earlier, the characteristic peaks were identified by careful comparison with standards. The definition of the retention index was then used to compute the indices of the various characteristic peaks. The value of "b" was determined and the computed retention indices were used as references for the computation of indices for the other fragments.

A complication results from the use of a hydrogen flame ionization detector. As illustrated in Figure 43, it is essential to employ adjusted retention parameters if "b" is expected to be a constant. To obtain an adjusted retention parameter, the peak position is measured from a non-retained peak, usually air, rather than the point of injection. Since the flame detector is not sensitive to air, a non-retained peak is not displayed.

To solve this problem, peak retention distances for the fragments in the breakdown patterns and those used to compute retention indices for the reference peaks were measured from the initial retention distances (the point where the leading edge of the peak just leaves the baseline) of methane. Since, under the conditions employed, this is only approximately equal to the position of a non-retained peak, the reported indices are referred to as "apparent" (Table 15).

Such a procedure for calculating retention indices has certain advantages. Since methane is reported to be present

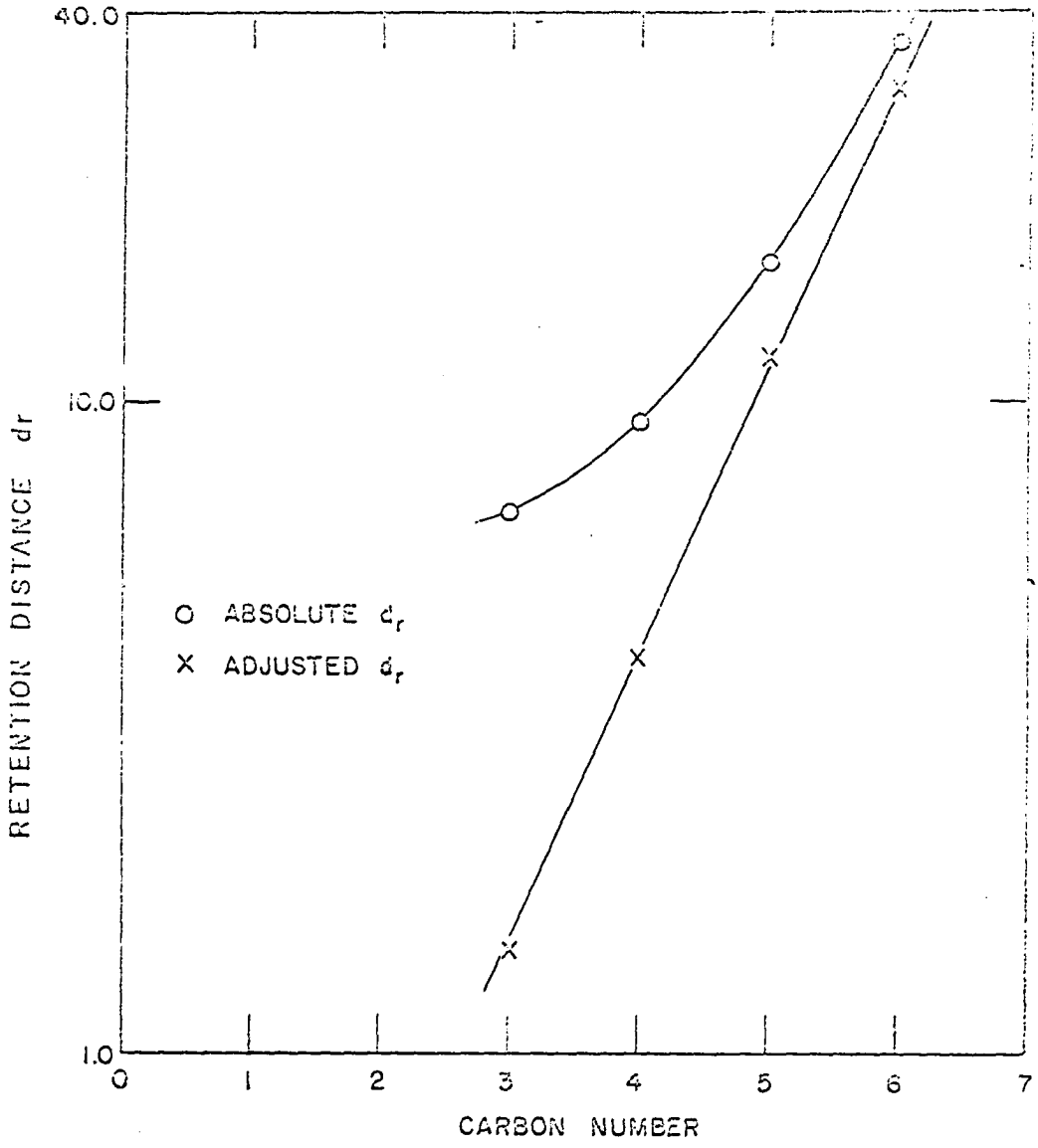

Figure 43. Absolute and adjusted retention distances of propane n-butane, n-pentane and n-hexane as a function of the number of carbon atoms in each n-alkane

in virtually all fragmentation patterns, the procedure is generally applicable. Since it would be expected that different sample types would yield greatly differing amounts of methane, it is desirable to use a retention position insensitive to sample size as the reference point. Initial retentions have been found to be much less dependent upon sample size than peak retentions (38,72).