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COMPARATIVE GAS CHROMATOGRAPHIC RESPONSE OF ORGANOPHOSPHORUS COMPOUNDS CONTAINING NITROGEN AND NITROGEN COMPOUNDS WITH ALKALI FLAME AND ELECTROLYTIC CONDUCTIVITY DETECTORS

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SUMMARY

Both the alkali flame detector and the electrolytic conductivity detector can be used for the gas chromatographic determination of nitrogen compounds. While the electrolytic conductivity detector is specific, the alkali flame detector responds to various hetero atoms. The response for a series of organonitrogen and organophosphorus compounds containing other hetero atoms were determined under the same experimental conditions, and the results were compared.

The response of the alkali flame detector is greater for phosphorus than for nitrogen and the results obtained suggest that the magnitude of response is dependent on structural effects. In the absence of phosphorus, compounds containing only nitrogen showed no obvious structural correlation. With the electrolyte conductivity detector the response is purely a function of the amount of nitrogen in the molecule. The responses of these two detectors to nitrogen compounds were of the same order.

INTRODUCTION

The analysis of nitrogen-containing compounds such as insecticides and herbicides can be achieved by the use of an alkali flame detector¹ (AFD) and a Coulson electrolytic conductivity detector (CCD)². Although a direct comparison under standard gas chromatographic (GC) conditions has not been reported, it appears, from published data^{2,3} that the AFD is more sensitive to nitrogen than the CCD. The response of the AFD depends on its design and on parameters such

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as gas flow-rates, electrode spacing, alkali salt used, and condition of the salt surface⁴. An important difference between the two detectors is that the AFD responds to various hetero atoms⁵ whereas the CCD can be made specific for nitrogen compounds.

The response of both detectors to some phosphates, phosphorothioates containing nitrogen, phosphoramidates, triazines, amides, and a carbamate was determined under identical GC conditions. The effect of the structure of these compounds on detector response is discussed and the relative merits of the Pye AFD and CCD are mentioned with particular emphasis on the determination of P,N- and N-containing pesticides at the residue level.

EXPERIMENTAL

Compounds

Samples of pesticides, herbicides, amides, and the carbamate were of analytical grade. The phosphoramidates were prepared by reaction of the respective phosphoramidochlorides with phenols and amines in the presence of NaH. The products were characterised by NMR and GC following purification by vacuum distillation. All had a purity > 98.5% by microanalytical and gas chromatographic analysis.

Methods

GC conditions. A Pye Series 104, Model 154 gas chromatograph equipped with an alkali flame detector (AFD) which had a rubidium chloride annulus and a Microtek MT 220 fitted with a Coulson electrolytic conductivity detector (CCD) Model C 321 were used. The quartz reduction tube, used in the latter, was packed with a nickel catalyst, and a strontium hydroxide acid-absorber was placed in the exit end of the reduction tube. The same length columns and packings were employed for both instruments, *i.e.* 3 ft. × 1/4 in. glass columns containing 100–120 mesh Gas-Chrom Q coated with 3% OV-17. The columns were conditioned at 250° for 1 h with gas flow, then at 340° for 4 h with no gas flow and finally at 250° overnight with gas flow. The operating parameters of the gas chromatographs and detectors are given in Table I. The signal of the AFD was attenuated (20×10^2) in order to give a baseline similar to that of the CCD at an attenuation of 1. This enabled the same parameters to be used for the digital integrator.

TABLE I
GAS CHROMATOGRAPHIC PARAMETERS

<i>GC equipment</i>	<i>AFD</i>	<i>CCD</i>
<i>Temperature (°C)</i>		
Column	200	200
Inlet	200	224
Detector	200	870 (pyrolyser)
<i>Flow-rates (ml/min)</i>		
Column	40 (nitrogen)	40 (helium)
Hydrogen	37	100
Air	275	
Sweep		60 (helium)

Procedure. The sample size was limited to 1 ng for organophosphorus compounds and to 50 ng for the other nitrogen-containing compounds to ensure that the detectors were operating within their linear range. Each injection comprised of 1 μ l hexane, 2 μ l solution, and 1 μ l air. Five replicates were carried out for each compound. The peak areas were measured by an Infotronics Model CRS 208 digital integrator using the same parameters for both detectors and expressed as counts. The precision (relative standard deviation) of the replicate injections averaged 3.1 % for the AFD and 4.0 % for the CCD.

RESULTS AND DISCUSSION

The Pye thermionic detector has three electrodes and is normally equipped with a cesium bromide (CsBr) annulus. For these experiments, however, a rubidium chloride (RbCl) annulus was substituted. The responses of phosphorus and nitrogen compounds were similar for both alkali salts with this detector, but the RbCl annulus was less noisy, more stable, and had a longer life span⁶. In addition, the use of chloride salts has been reported to suppress the response to halogens⁷. When the Pye detector was adjusted for the determination of phosphorus and nitrogen, the response to sulphur and chlorine could be ignored. Thus, 1 μ g of Lindane (1,2,3,4,5,6-hexachlorocyclohexane) gave only a small negative peak whilst 1 μ g of Tetrasul (2,4,5,4-tetrachlorodiphenyl sulphide) produced no response.

In this work it is assumed that the peak area is independent of the retention time and peak shape. Under the same GC conditions, the retention time was less with the AFD than the CCD due to the longer transfer line and the pyrolyser. As noted, some determinations involving the AFD were run at a lower temperature (195°) which resulted in a slight change of the sensitivity of this detector.

The AFD response per mole of some organophosphorus compounds is given in Table II. This includes a comparison of phosphates and phosphorothioates (section A), phosphoramidates differing in the number of nitrogen atoms substituted on the phosphorus (section B), and finally, phosphorothioates in which the position and the amount of nitrogen in the molecule is varied (section C).

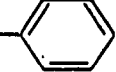
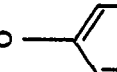
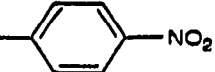
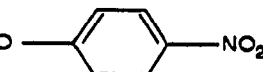
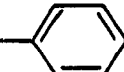
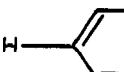
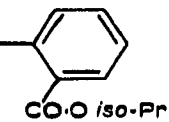
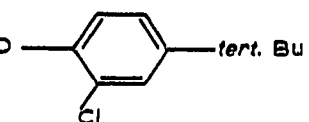
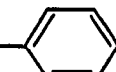
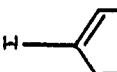
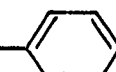
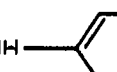
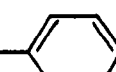
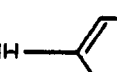
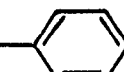
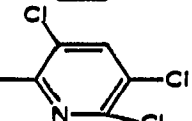
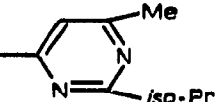
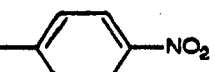
From these results it appears that the structure of the compound affects the response of this detector. Cross-table comparison (Table II, section A) shows that in all cases the phosphorothioates (P = S) have a greater response per mole than the corresponding phosphates. With the phosphoramidates (Table II, Section B), two main effects are noticed. First, replacement of a P-OC bond by P-NC reduces the response; the greater the number of P-N bonds in the molecule, the greater the effect. Second, the reduction in the response per mole is greater for N-aryl than N-alkyl compounds. Finally, in those phosphorothioates where the nitrogen atom in the molecule is separated by two or more bonds from the phosphorus (Table II, Section C) the response appears to be slightly enhanced.

Little is known of the mechanism of detection by alkali flame. It has been suggested that the combustion of organophosphorus compounds in an oxygen environment results in the formation of active species which further react with hydrogen atoms in the flame when in the presence of alkali metal atoms⁸. The detector response must be related to energy factors involved in these reactions, which in turn may be related to the energy of the phosphorus compound in the ground state or the activated state.

TABLE II

RESPONSE OF THE AFD TO SOME ORGANOPHOSPHATES, PHOSPHOROTHIOATES, AND PHOSPHORAMIDATES

Section A: phosphorothioates-phosphates; section B: phosphoramidates with various N-atoms substituted on P; section C: phosphorothioates with various N substituted on various positions.

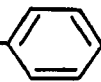
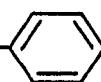
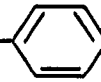
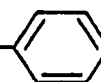
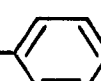
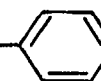
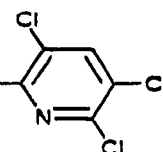
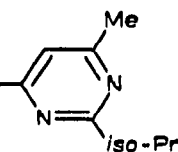
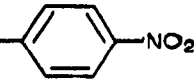
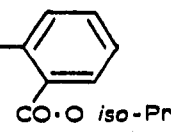
Compound	Response ^a (counts/ pmole)	Compound	Response ^a (counts/ pmole)
Section A			
EtO EtO P(S) O- 	3720 ^b	EtO EtO P(O) O- 	2824 ^b
EtO EtO P(S) O- 	4360	EtO EtO P(O) O- 	2250
EtO EtO P(S)NH- 	3070 ^b	EtO EtO P(O) NH- 	1982 ^b
MeO NH ₂ P(S) O- 	3732	MeO MeNH P(O) O- 	2723
Section B^b			
EtO EtO P(O) O- 	2824	EtO EtO P(O) NH- 	1982
NMe ₂ EtO P(O) O- 	2426	NMe ₂ EtO P(O) NH- 	1690
NMe ₂ NMe ₂ P(O) O- 	2290	NMe ₂ NMe ₂ P(O) NH- 	1536
Section C^b			
EtO EtO P(S) O- 	4308		
EtO EtO P(S) O- 	4700		
EtO EtO P(S) O- 	5691		
EtO EtO P(S) O- 	4366		

^a Response = peak area/mole = (counts/mole) · 10¹² = counts/pmole.

^b Column and detector temperature = 195°.

TABLE III

RESPONSE OF THE CCD TO ORGANOPHOSPHORUS COMPOUNDS CONTAINING NITROGEN

Compound	Response ^a	
	Counts/pmole	Counts/pmole/N
NMe ₂ EtO P(O) O- 	31.28	31.28
NMe ₂ NMe ₂ P(O) O- 	66.17	33.08
EtO EtO P(O) NH- 	33.07	33.07
NMe ₂ EtO P(O) NH- 	56.31	28.15
NMe ₂ NMe ₂ P(O) NH- 	88.69	29.56
EtO EtO P(S) O- 	—	—
EtO EtO P(S) O- 	30.83	30.83
EtO EtO P(S) O- 	66.68	33.36
EtO EtO P(S) O- 	34.19	34.19
MeO NH ₂ P(S) O- 	32.11	32.11

^a Response = peak area/mole = (counts/mole) · 10¹² = counts/pmole.

The results in Table II indicate that the response per mole for phosphorothioates is greater than for phosphates, and phosphates greater than for phosphoramidates. Since the bond energies are in the order $P-OC > P-NC$ and $P=O > P=S^0$, it appears there is no correlation between response and bond energies in the ground state.

In case of the CCD, organonitrogen compounds are pyrolysed and hydrogenated over a nickel catalyst at 870° in a quartz tube. This results in the formation of ammonia which is selectively detected. The estimated overall efficiency has been reported¹⁰ at 70–80%. The major reasons for low efficiency are incomplete conversion of organonitrogen compounds to ammonia and losses on the GC column. The CCD can in fact be made selective to amines by lowering the temperature to 400–600° and removing the catalyst when pyrolysis rather than hydrogenation occurs. Amine type compounds can thereby be detected in the presence of large amounts of other N-containing materials¹¹.

The CCD results in Table III for the organophosphorus compounds containing nitrogen, show an average value of 31.03 ± 3 (counts/pmole/N). This is less by a factor of *ca.* 100 when compared with the results for the AFD response. A similar factor was found by EBERLE AND HÖRMANN¹² when they determined the response of Supracide by AFD and CCD.

When the responses of the Pye AFD and CCD are compared for compounds which contain nitrogen but no phosphorus, as in Table IV, it can be seen that the response is slightly greater for the CCD.

The CCD response per mole N is scattered but an average value of 33.4 ± 4.6 (counts/pmole/N) was found for the triazines, which is quite close to that obtained for the organophosphorus compounds containing nitrogen already mentioned above. This average value is also good for the remaining compounds examined except for diphenamid. In an earlier study¹³ it was observed that the substituted urea herbicides possessing the $-CO-N(Me)_2$ moiety (as does diphenamid) exhibited half the area response when compared to equivalent amounts of nitrogen for $-CO-N(OMe)Me$ containing compounds. On-column decomposition as an explanation was ruled out as no other products were detected and it is believed that these low results were due to unfavourable hydrogenation conditions.

In the case of the AFD the response per mole is more varied. Apart from atrazine, the triazines give an average value of 13.3 counts/pmole/N which is approximately twice that obtained for trifluralin, Azak, diphenamid, and propanil. Therefore, unlike the CCD, no uniform response per mole N appears to exist.

Although the response of the AFD and CCD are of the same order under the experimental conditions used here, the response per mole N of the AFD is much more variable. Even with a RbCl annulus, the absolute response of this detector still depends on precise control of the hydrogen flow in order that the same position is maintained on the response/hydrogen-flow curve, and on the degree of contamination of the alkali surface¹⁴. For routine analysis of compounds containing N only, the CCD is preferred for its selectivity and ease of operation. For organophosphorus compounds containing nitrogen, the AFD is better. In this work the OV-17 liquid phase substrate proved to be thermally stable¹⁵ resulting in little or no contamination of the alkali salt surface or the CCD detector cell¹³.

TABLE IV

RESPONSE OF THE AFD AND CCD TO SOME TRIAZINES, CARBAMATES AND AMIDES

Compound ^a	AFD		CCD		
	Counts/ μmole^b	Counts/ $\mu\text{mole}/N$	Counts/ μmole^b	Counts/ $\mu\text{mole}/N$	
Atrazine		106.30	21.2	172	34.6
Atratone		68.38	13.6	147	29.5
Ametryne		65.04	13.0	169.69	33.6
Outfox		56.08	14.0	124	31.7
Sencor		51.08	12.8	124	31.7
Dichlorfuanid		30.90	15.4	68.59	34.3
Trifluralin		26.26	8.78	98.95	32.9
Ramrod		13.96	13.96	34.98	34.98
Azak		7.26	7.26	27.21	27.21
Diphenamid		5.72	5.72	20.14	20.14
Propanil		6.36	6.36	27.00	27.00

^a R' = -NH Et; R'' = -NH iso-Pr.^b Response = peak area/mole = (counts/mole) · 10¹² = counts/ μmole .

CONCLUSION

In summary, the response per mole of different organophosphorus compounds using the AFD varies sufficiently to suggest that response is influenced by the structure of molecules containing both phosphorus and nitrogen. For routine analysis of nitrogen compounds by GC the CCD is preferred, and if phosphorus is also present in the molecule, then the AFD is preferred because of its greater sensitivity.

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