Pyrolytic Sulfurization Gas Chromatography. XV. Simultaneous Determination of the Atomic Ratio between C, H, O, and N in an Organophosphorus Compound

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In order to confirm whether or not pyrolytic sulfurization gas chromatography can be applied to organophosphorus compounds, many kinds of organophosphorus compounds were examined; C-rich compounds gave satisfactory results while C-poor ones gave lower oxygen values. The application limit of this method to various organophosphorus compounds was determined by the use of the C/O value and a structural factor for a sample, and the application limit was established. The structural factor of a sample varied with the kind of X_1, X_2, X_3, and X_4 in the general formula $X_1X_2X_3P=X_4$, where X_1=OH, OR, R; X_2=OH, OR′, R′; X_3=OH, OR″, R″; and X_4=O, S.

With the objective of establishing a new organic elemental analysis method by which several elements can be simultaneously determined, pyrolytic sulfurization gas chromatography (PSGC) was originated[1] and has been studied[2–14] by the authors. The PSGC method is based on a combustion technique in sulfur vapor instead of the conventional one in an oxygen atmosphere; this makes possible the simultaneous determination of the atomic ratio between C, H, O, and N in an organic compound without weighing the sample. So far this method has been successfully applied to a normal organic compound,[1,2] a metal organic chelate,[3,13] a polymer,[5] and an organic halogen compound.[7,9]

In the field of conventional organic elemental analysis, oxygen in an organic compound containing metallic or non metallic elements cannot be analyzed with ease because a number of elements show a strong affinity for oxygen and are apt to form nonvolatile compounds such as their oxides or carbonates. On the contrary, the PSGC method makes possible the simultaneous determination of the atomic ratio between C, H, O, and N even in a compound containing the above-mentioned elements because they are converted into their sulfides. Though the effects of many coexistent elements on the determination of C, H, O, and N have been discussed and clarified, the effect of phosphorus as a coexistent element still remained unsolved in the previous studies.[3,13] Moreover, the determination of oxygen in an organophosphorus compound by the conventional organic elemental analysis method is difficult. Therefore, the present study has been carried out to confirm whether or not the PSGC method can be applied to various types of organophosphorus compounds. Fifteen kinds of organophosphorus compounds were analyzed by the PSGC method; C-rich compounds gave satisfactory results but C-poor ones gave low oxygen values. This was explained by the assumption that the phosphorus oxides produced from phosphorus and oxygen in a sample are reduced to phosphorus sulfide by carbon in a C-rich compound sample, but not in a C-poor compound sample. On the other hand, some experimental results could not be explained by the C/O value alone. In these cases, the application limit of the PSGC method to various organophosphorus compounds was decided by the use of the C/O value and a structural factor for the sample. The structural factor of a sample varied with the kind of X_1, X_2, X_3, and X_4 in the general formula $X_1X_2X_3P=X_4$ where X_1=OH, OR, R; X_2=OH, OR′, R′; X_3=OH, OR″, R″; and X_4=O, S.

Experimental

Apparatus and Reagents. The apparatus and reagents used in this experiment were the same as those reported previously. A definite amount of sample was taken using a Shimadzu microbalance MDP-5.

Samples. Eleven kinds of organophosphorus compounds, sample numbers 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, and 12 (shown in Table 1) were synthetic ones provided by Professor Isao Furukawa at Doshisha University. Other samples were of reagent grade. These samples were, if necessary, purified by recrystallization from appropriate solvents. The composition and purity of the samples were confirmed by CH and/or CHN analysis carried out in the Elemental Analysis Center of the Pharmaceutical Department of Kyoto University (Table 1).

Procedure. A 0.3—0.5 mg of sample and 5 mg of purified sulfur[4] was inserted into a quartz tube (2.5 mm i.d., 3.5 mm o.d., and 100 mm long), one end of which was previously closed. The air inside the tube containing the sample and S was displaced with He for 10 min at the flow rate of 100 cm^3/min, followed by sealing the other end of the tube. The ampule thus obtained was treated for 10 min at 600 °C and for 30 min at 950 °C. The reaction products, carbon dioxide, carbonyl sulfide, carbon disulfide, hydrogen sulfide, and nitrogen, in the ampule were analyzed gas-chromatographically by crushing the ampule in the flow of the gas chromatograph, followed by calculation of the atomic ratio between C, H, O, and N in the sample in the same way as that reported previously.[2] The precision of the PSGC had been reported in the previous paper.[14]

Results

Analytical Results of Various Organophosphorus Compounds. Various organophosphorus compounds were analyzed by the PSGC method; the results are shown in Table 2. As can be seen from Table 2, C-rich compounds gave satisfactory results, but C-poor compounds such as samples 11, 13, 14, and 15 did not. In the PSGC

TABLE 1. ANALYTICAL RESULTS OF C, H, AND N IN AN ORGANOPHOSPHORUS COMPOUND

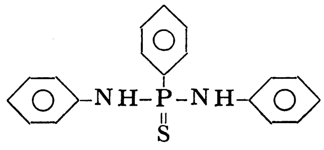
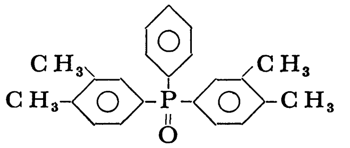
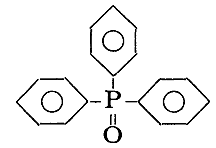
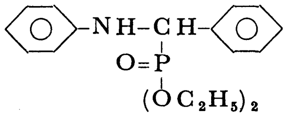
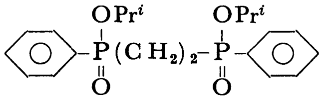
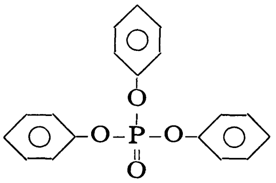
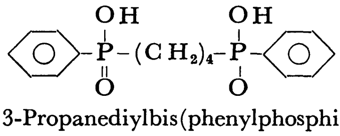
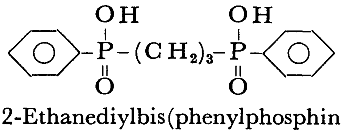
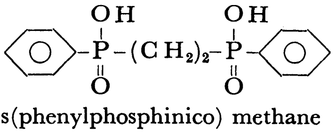
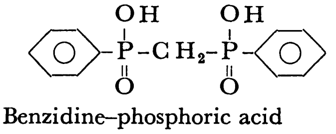
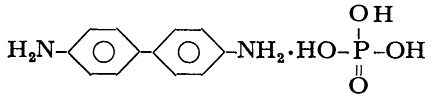
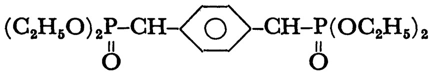
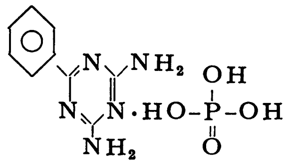
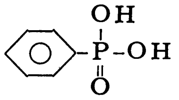
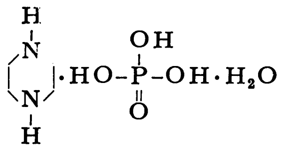
Sample No.	Sample	C (wt%)			H (wt%)			N (wt%)		
		Calcd	Found	Error	Calcd	Found	Error	Calcd	Found	Error
1	*N,N'*-Diphenylphenylphosphonothioic diamide 	66.65	66.47	−0.18	5.28	5.33	+0.05	8.64	8.39	−0.25
2	Bis(3,4-dimethylphenyl) phenylphosphine oxide 	79.02	78.86	−0.16	6.93	7.16	+0.23			
3	Triphenylphosphine oxide 	77.69	77.53	−0.16	5.43	5.34	−0.09			
4	Diethoxy(α-anilinobenzyl) phosphine oxide 	63.94	64.08	+0.14	6.94	7.17	+0.23	4.39	4.29	−0.10
5	1,2-Bis(isopropoxyphenylphosphinyl)ethane 	60.91	60.62	−0.29	7.16	7.06	−0.10			
6	Triphenyl phosphate 	66.26	66.16	−0.10	4.63	4.62	−0.01			
7	1,4-Butanediylbis(phenylphosphinic acid) 	56.81	56.66	−0.15	5.96	6.01	+0.05			
8	1,3-Propanediylbis(phenylphosphinic acid) 	55.56	55.40	−0.16	5.60	5.63	+0.03			
9	1,2-Ethanediylbis(phenylphosphinic acid) 	54.20	54.29	+0.09	5.20	5.24	+0.04			
10	Bis(phenylphosphinico) methane 	52.72	52.48	−0.24	4.76	4.62	−0.14			
11	Benzidine–phosphoric acid 	51.07	51.03	−0.04	5.36	5.33	−0.03	9.93	10.01	+0.08

Table 1. (Continued)

Sample No.	Sample	C (wt%)			H (wt%)			N (wt%)		
		Calcd	Found	Error	Calcd	Found	Error	Calcd	Found	Error
12	*p*-Xylene-α,α′-diylbis(diethoxyphosphine oxide) 	50.79	50.90	+0.11	7.46	7.73	+0.27			
13	Benzoguanamine–phosphoric acid 	37.90	37.97	+0.07	4.24	4.32	+0.08	24.56	24.72	+0.16
14	Phenylphosphonic acid 	45.58	45.86	+0.28	4.46	4.47	+0.01			
15	Piperazine–phosphoric acid–water 	23.77	23.61	−0.16	7.48	7.60	+0.12	13.86	13.89	+0.03

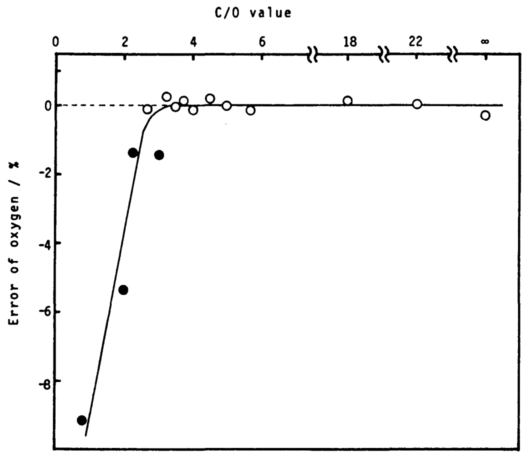


Fig. 1. Relationship between error of oxygen and C/O value in a organophosphorus compound.
○: Applicable compound and ●: not applicable one.

method, each content of C, H, O, and N in a sample is calculated by normalizing their total contents to 100%. In order to clarify which element was influenced by phosphorus as a coexistent element, the atomic ratios of H, O, and N to C were calculated; it became apparent that only the content of O was influenced by phosphorus. This may be explained by the assumption that phosphorus oxide produced from phosphorus and oxygen in a sample is reduced by carbon in a C-rich compound sample, but not in a C-poor compound sample. The white powder, which was presumed to be a phosphorus oxide, was observed in the ampule of the latter case after pyrolytic sulfurization.

Relationship between the Analytical Results and the C/O Value. The atomic ratio of C to O (the C/O value) was defined as an indication of the reducing power for the phosphorus oxide to explain the above-mentioned results. The relationship between the error of oxygen in each analytical result of organophosphorus compound and the C/O value calculated from each sample was shown in Fig. 1. Figure 1 shows that the PSGC method can be applied to organophosphorus compounds in which the C/O value exceeds about 3 and the negative error in oxygen value increases with a decreasing C/O value less than about 3. However, the fact that sample 11 (C/O=3.0) did not give a satisfactory result while sample 12 (C/O=2.7) did give a satisfactory result cannot be explained by the C/O value alone. Therefore, another factor must also be taken into consideration to clarify the application limit of the PSGC method to organophosphorus compounds. It is discussed below.

Discussion

Effect of the Chemical Structure of a Sample on the Analytical Result. Since the application limit of the PSGC method to organophosphorus compounds could not be decided exactly by the C/O value alone as mentioned above, the chemical structure of a sample was investigated as another factor of deciding the application limit to organophosphorus compounds in which the oxidation number of phosphorus is +5 in the following manner. Three kinds of mixed samples with the C/O values of 1—7 were prepared as model compounds by the use of the following pairs; sample 1 and sucrose, sample 5 and sucrose, and sample 15 and anthracene, respectively. These samples were analyzed by the PSGC method; each relationship between the analytical value of oxygen in each sample and its C/O value is shown in Fig. 2, where all analytical values of C, H, and N were

Table 2. Analytical results for various organophosphorus compounds

Sample No.	Sample	C/O	C (wt%) Calcd	C (wt%) Found	C (wt%) Error	H (wt%) Calcd	H (wt%) Found	H (wt%) Error	O (wt%) Calcd	O (wt%) Found	O (wt%) Error	N (wt%) Calcd	N (wt%) Found	N (wt%) Error
1	*N*,*N'*-Diphenylphenylphosphonothioic diamide	∞	82.72	82.82	+0.10	6.56	6.78	+0.22				10.72	10.40	−0.32
2	Bis(3,4-dimethylphenyl)phenylphosphine oxide	22	87.09	87.08	−0.01	7.64	7.62	−0.02	5.27	5.30	+0.03			
3	Triphenylphosphine oxide	18	87.42	87.34	−0.08	6.11	6.06	−0.05	6.47	6.60	+0.13			
4	Diethoxy(α-anilinobenzyl)phosphine oxide	5.7	70 81	70.89	+0.08	7.69	7.67	−0.02	16.64	16.50	−0.14	4.86	4.94	+0.08
5	1,2-Bis(isopropoxyphenylphosphinyl)ethane	5.0	72.26	72.35	+0.09	8.49	8.43	−0.06	19.25	19.22	−0.03			
6	Triphenyl phosphate	4.5	73.21	73.06	−0.15	5.12	5.07	−0.05	21.67	21.87	+0.20			
7	1,4-Butanediylbis(phenylphosphinic acid)	4.0	69.54	69.72	+0.18	7.30	7.26	−0.04	23.16	23.02	−0.14			
8	1,3-Propanediylbis(phenylphosphinic acid)	3.8	68.68	68.41	−0.27	6.92	7.06	+0.14	24.40	24.53	+0.13			
9	1,2-Ethanediylbis(phenylphosphinic acid)	3.5	67.72	67.73	+0.01	6.50	6.51	+0.01	25.78	25.76	−0.02			
10	Bis(phenylphosphinico)methane	3.3	66.66	66.40	−0.26	6.02	6.04	+0.02	27.32	27.56	+0.24			
11	Benzidine–phosphoric acid	3.0	57.36	58.73	+1.37	6.02	6.11	+0.09	25.47	24.04	−1.43	11.15	11.12	−0.03
12	*p*-Xylene-α,α'-diylbis(diethoxyphosphine oxide)	2.7	60.74	60.96	+0.22	8.92	8.81	−0.11	30.34	30.23	−0.11			
13	Benzoguanamine–phosphoric acid	2.3	42.52	43.29	+0.77	4.76	4.92	+0.16	25.17	23.79	−1.38	27.55	28.00	+0.45
14	Phenylphosphonic acid	2.0	56.69	61.42	+4.94	5.55	5.97	+0.42	37.76	32.40	−5.36			
15	Piperazine–phosphoric acid–water	0.8	28.07	34.12	+6.05	8.83	10.34	+1.51	46.73	37.57	−9.16	16.37	17.97	+1.60

Table 3. Applicable region of the PSGC method PSGC method to organophosphorus compounds

Structure	$X_1X_2X_3P=X_4$				C/O										
	X_1	X_2	X_3	X_4	0	1	2	3	4	5	6	7	18	22	∞
A	OH	OH	OH	O		−	−	−							
B	OH	OH	OR	O											
C	OH	OH	R	O			−								
D	OH	OR	OR	O											
E	OH	OR	R	O											
F	OH	R	R	O					++++						
G	OR	OR	OR	O					+						
H	OR	OR	R	O				+			+		+		
I	OR	R	R	O						+					
J	R	R	R	O										+	
K	R	R	R	S											+

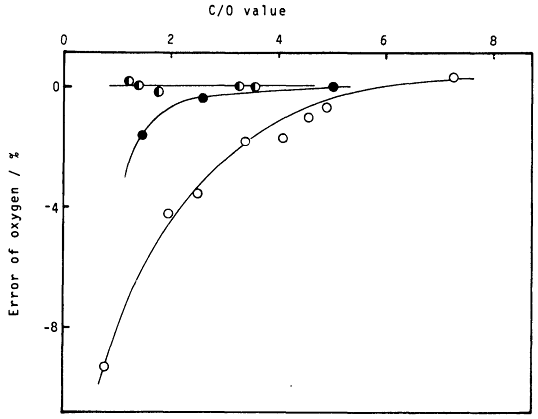


Fig. 2. Relationship between error of oxygen and C/O value in a mixed sample.
○: Sample 15 and anthracene, ●: sample 5 and sucrose, and ◐: sample 1 and sucrose.

confirmed to be correct from the atomic ratios of H and N to C. As can be seen from Fig. 2, the errors of oxygen decrease with an increasing C/O value, but the numerical values of the oxygen error are different from one another even at the same value of C/O. This is attributed to the difference of the chemical structure of the sample, that is, satisfactory results are obtained for the following samples; 1) sample 15 as an addition compound of phosphoric acid when the C/O value is more than 5.5, 2) sample 5 as a derivative of phosphinic acid when the C/O value is more than 2, and 3) sample 1 as a derivative of phosphonothioic acid containing no oxygen when the C/O value is more than 1. Thus the analytical result of oxygen is influenced by the substituent groups bonding to phosphorus, -OH, -OR, and -R (R indicates a hydrocarbon group), in that order. From the results of this experiment, the application limit of the PSGC method to organophosphorus compounds may be explained by the use of two factors; the C/O value and the chemical structure.

Application Limit of the PSGC Method to Organophosphorus Compounds. In order to clarify the application limit of the PSGC method to organophosphorus compounds, the relationship between each analytical result of organophosphorus compound and above-mentioned two factors was investigated; the results are shown in Table 3. In Table 3, substituent groups bonding to phosphorus (V) as a structural factor are vertically enumerated in the order of their interferences and the C/O values are arranged horizontally, followed by marking + at the corresponding position for the sample giving a satisfactory result and by marking — for one giving a negative error of oxygen. In addition, both the positions giving satisfactory results for phosphoric acid, C/O=5.5 in structure A, and for phosphonothioic acid, C/O=1 in structure J, were linked with a broken line. This broken line indicates the application range of the PSGC method, that is, the sample satisfying the conditions under the broken line may be analyzed by the PSGC method without any exceptions.

Judging from the results obtained by the present study and the difficulties in oxygen analysis of an organophosphorus compound by the conventional method, the utility of the PSGC method in analysis of an organophosphorus compound is obvious even though its applicable region is restricted by the application limit.

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