Pyrolytic Sulfurization Gas Chromatography. IX. Determination of the Atomic Ratio between C, H, O, N, Cl, Br, and I in an Organic Halogen Compound

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The atomic ratio between C, H, O, N, Cl, Br, and I in an organic halogen compound was obtained satisfactorily by gas chromatography and ion chromatography. At first the atomic ratio between C, H, O, and N was determined simultaneously by PSGC and then the atomic ratio between a halogen atom and C, H, O, and N was obtained by estimating the amount of a halogen atom in the reaction residue and by calculating the weight percent in Eq. 4 by use of a correction factor and peak areas in gas and ion chromatograms.

Pyrolytic sulfurization gas chromatography (PSGC), which was originated by the present authors, has been successfully applied to the simultaneous determination of the atomic ratio between C, H, O, and N in a normal organic compound,[1] a metal organic chelate compound,[2] a polymer,[3] and an organic halogen compound.[4]

The present study has been further carried out with the objective of estimating the atomic ratio between C, H, O, N, and halogen atoms (Cl, Br, and I) (X) in an organic halogen compound. Since X in an organic halogen compound was fixed in the reaction residue as sodium halide (NaX) by PSGC,[4] determination of X in the NaX was separately investigated by (1) gas chromatography after conversion of the halide to hydrogen halide (HX) and (2) ion chromatography after dissolving the halide in water, and the results obtained were compared. In the former, HX was easily identified but its determination was difficult due to the incomplete conversion of the NaX to HX and the decomposition of HX. In the latter, a satisfactory result was obtained by dissolving the reaction residue with an aqueous solution of potassium hydrogen phthalate (KHP), by filtering S and quartz pieces off, and by introducing the filtrate to an ion chromatograph through a Teflon membrane filter. On the basis of the relationship between the peak of hydrogen sulfide (H_2S) in a gas chromatogram and that of halide ions (X^-) in an ion chromatogram for a definite composition of organic halogen compound, the atomic ratio of H to X for an unknown compound was obtained without weighting it.

Experimental

Apparatus and Samples. The same gas chromatograph was used as described in the previous paper. A HITACHI 634A liquid chromatograph fitted with a Wescan model 213 conductivity detector and Vydac 302 IC 4.6 column (250 mm), was operated at the flow rate of 1.7 cm^3/min by use of a 0.004 mol/dm^3-KHP as an eluent to monitor X^-.

The organic halogen compound samples were of analytical grade.

Procedure. The ampule containing an organic halogen compound, S, and sodium sulfide (Na_2S) was made to react by the previously described procedure.[4] It was placed in a 80 mm long, 4.22 mm i.d., 4.94 mm o.d. Teflon tube, and crushed in a gas sampler, the evolved gases being analyzed in accordance with the previous paper to determine the atomic ratio between C, H, O, and N. The pieces obtained by crushing the ampule was taken out of the sampler and treated with 0.004 mol/dm^3-KHP, followed by filtration through a G4 glass filter. The filtrate was passed through a Teflon membrane filter (pore size 0.5 μm) and introduced into an ion chromatograph. According to the present procedure, well-defined and separated peaks were obtained for X^- and they were used for the determination of the atomic ratio between C, H, O, N, and X.

Results and Discussion

Analysis of X^- by Ion Chromatography. A mixed solution consisting of each 5×10^{-4} mol/dm^3 sodium chloride, sodium bromide, and sodium iodide was analyzed by ion chromatography under the above-mentioned conditions. As can be seen from Fig. 1, the present procedure gives a satisfactory result for the

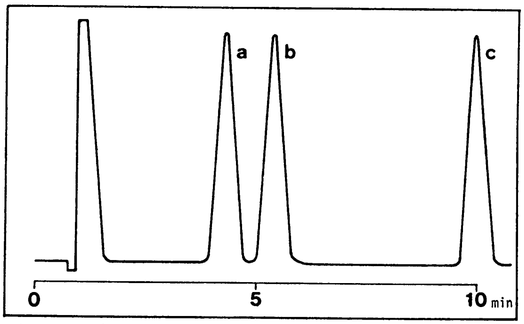

Fig. 1. Typical chromatogram of halogen atoms by the ion chromatography.
a): Cl$^-$, b) Br$^-$, c): I$^-$.
Conditions: Column Vydac 302 IC 4.6 (250 mm); detector conductivity (Wescan model 213); eluent 0.004 mol/dm^3-KHP; flow rate 1.7 cm^3/min.

TABLE 1. PRECISION[a] IN THE DETERMINATION OF HALIDE IONS BY ION CHROMATOGRAPHY

Ions	C.V. (%)
Cl$^-$	2.133
Br$^-$	1.203
I$^-$	1.814

a) 10 runs for the standard solution. (5×10^{-4} mol/dm^3-NaCl, -NaBr, -NaI)

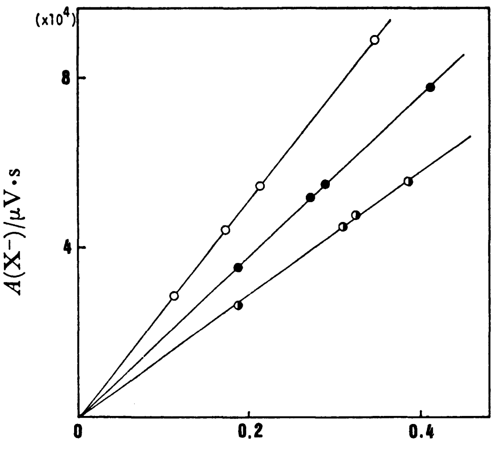

Fig. 2. Relationship between sample weight and $A(X^-)$.
○: *p*-Chlorobenzoic acid, ●: *p*-bromoacetanilide, ◑: *o*-iodobenzoic acid.

separation of X^-. In order to examine the precision of the present procedure, each 5×10^{-4} mol/dm^3 standard solution of X^- was analyzed 10 times and the results were shown in Table 1 by the coefficient of variation (C.V.). The values of C.V. in Table 1 are reasonable ones in comparison with those obtained by an ordinary ion chromatography.

Determination of X by Use of Calibration Curve. Three kinds of organic halogen compounds, that is, 0.112—0.350 mg *p*-chlorobenzoic acid, 0.188—0.416 mg *p*-bromoacetanilide, and 0.188—0.390 mg *o*-iodobenzoic acid were analyzed by the above-mentioned procedure and the relationship between sample weight and peak area in an ion chromatogram were plotted in Fig. 2. Judging from the linearity in Fig. 2, the present procedure is suitable for the determination of X in an organic halogen compound.

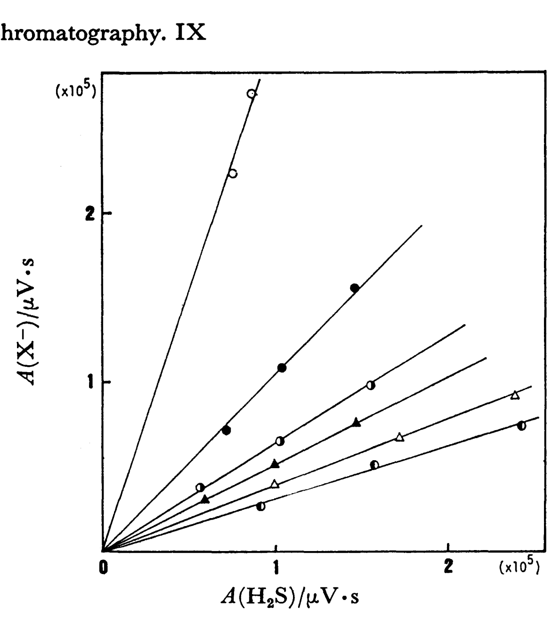

Fig. 3. Relationship between $A(H_2S)$ and $A(X^-)$.
○: 1,2,3,4,5,6-Hexachlorocyclohexane, ●: 1-chloro-2,4-dinitrobenzene, ◐: S-benzylthiouronium chloride, ◑: *p*-chlorobenzoic acid ▲: *p*-bromoacetanilide △: *o*-iodobenzoic acid.

To examine the recovery of the present procedure, a definite amount of organic halogen compound was treated by PSGC and the absolute value of X in it was determined using a calibration curve which had been obtained with a standard solution of NaX (Tables 2 and 3). As can be seen from Tables 2 and 3, satisfactory results were obtained for X. This means that both

Table 2. Analytical results of organic halogen compounds by use of a calibration curve

Sample	Weight (mg)	Halogen content			
		Theor. (mg)	Found (mg)	Found (%)	Error (%)
p-Chlorobenzoic acid	0.442	0.100	0.101	22.9	(+0.3)
S-Benzylthiouronium chloride	0.504	0.0881	0.0869	17.2	(−0.3)
1-Chloro-2,4-dinitrobenzene	0.477	0.0835	0.0838	17.6	(+0.1)
1,2,3,4,5,6-Hexachlorocyclohexane	0.289	0.216	0.216	74.7	(0)
α-Bromoisovarerylurea	0.350	0.125	0.127	36.3	(+0.5)
p-Bromoacetanilide	0.386	0.144	0.144	37.3	(0)
1,2,3,4,5,6-Hexabromocyclohexane	0.403	0.347	0.346	85.9	(−0.1)
o-Iodobenzoic acid	0.397	0.203	0.204	51.4	(+0.2)

Table 3. Analytical results of organic halogen compounds by use of a calibration curve

Sample	Weight (mg)	Cl			Br			I		
		Theor. (mg)	Found (mg)	Content (%) [Error]	Theor. (mg)	Found (mg)	Content (%) [Error]	Theor. (mg)	Found (mg)	Content (%) [Error]
p-Chlorophenacyl bromide	0.472	0.0716	0.0696	14.7 [−0.5]	0.162	0.164	34.8 [+0.5]			
5-Chloro-7-iodo-8-quinolinol	0.496	0.0575	0.0560	11.3 [−0.3]				0.206	0.205	41.3 [−0.2]
p-Bromoiodobenzene	0.486				0.137	0.135	27.8 [−0.4]	0.218	0.220	45.3 [+0.4]

TABLE 4. CORRECTION FACTOR OF X^-

Run No.	Ions	Correction factor[a]	C.V. (%)
1[b]	Cl^-	0.6765	2.011
2[c]	Br^-	0.6978	1.818
3[d]	I^-	0.6407	2.026

a) Average of 10 runs for the standard sample. b) 1-Chloro-2,4-dinitrobenzene. c) α-Bromoisovarerylurea. d) *o*-Iodobenzoic acid.

the fixation of X to the reaction residue by PSGC and the dissolution of NaX from the reaction residue are quantitative.

Calculation of the Atomic Ratio between C, H, O, N, and X. Six kinds of organic halogen compounds were analyzed by the present method, and the relationship between the peak area of H_2S in a gas chromatogram ($A(H_2S)$) and the peak area of X^- in an ion chromatogram ($A(X^-)$) was plotted in Fig. 3. Each relationship gives a straight line. The relationship between $A(H_2S)$ and $A(Cl^-)\times(H/Cl)$, which meant the product of the peak

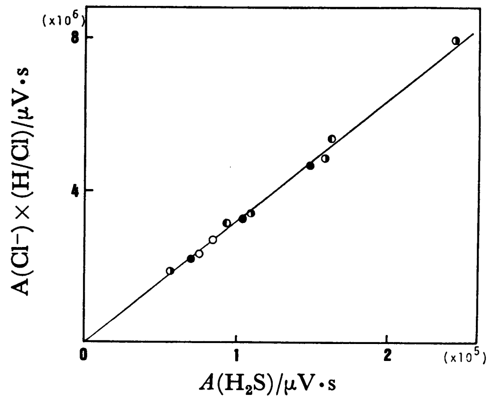

Fig. 4. Relationship between $A(H_2S)$ and $A(Cl^-)\times(H/Cl)$.
○: 1,2,3,4,5,6-Hexachlorocyclohexane, ●: 1-chloro-2,4-dinitrobenzene, ◐: S-benzylthiouronium chloride, ◑: *p*-chlorobenzoic acid.

TABLE 5. ANALYTICAL RESULTS OF ORGANIC HALOGEN COMPOUNDS

Sample	Content[a] (wt %)						
	C	H	O	N	Cl	Br	I
p-Chlorobenzoic acid	53.70	3.22	20.44		22.64		
	53.59	3.26	20.64		22.51		
	(−0.11)	(+0.04)	(+0.20)		(−0.13)		
S-Benzylthiouronium chloride[b]	56.30	6.50		16.42	20.78		
	56.24	6.41		16.46	20.89		
	(−0.06)	(−0.09)		(+0.04)	(+0.11)		
1,2,3,4,5,6-Hexachlorocyclohexane	24.78	2.08			73.14		
	25.09	2.12			72.79		
	(+0.31)	(+0.04)			(−0.35)		
1-Chloro-2,4-dinitrobenzene	35.58	1.49	31.60	13.83	17.50		
	35.91	1.48	31.39	13.82	17.40		
	(+0.33)	(−0.01)	(−0.21)	(−0.01)	(−0.10)		
1,2,3,4,5,6-Hexabromocyclohexane	12.93	1.08				85.99	
	12.60	1.09				86.31	
	(−0.33)	(+0.01)				(+0.32)	
α-Bromoisovarerylurea	32.31	4.97	14.34	12.56		35.82	
	32.55	4.91	14.53	12.50		35.51	
	(+0.24)	(−0.06)	(+0.19)	(−0.06)		(−0.31)	
p-Bromoacetanilide	44.89	3.77	7.47	6.54		37.33	
	45.03	3.71	7.33	6.59		37.35	
	(+0.14)	(−0.07)	(−0.14)	(+0.05)		(+0.02)	
o-Iodobenzoic acid	33.90	2.03	12.90				51.17
	34.12	2.00	12.79				51.09
	(+0.22)	(−0.03)	(−0.11)				(−0.08)
p-Chlorophenacyl bromide	41.16	2.59	6.85		15.18	34.22	
	40.96	2.45	6.76		14.81	35.02	
	(−0.20)	(−0.14)	(−0.09)		(−0.37)	(+0.80)	
5-Chloro-7-iodo-8-quinolinol	35.38	1.65	5.24	4.58	11.60		41.55
	35.80	1.67	5.29	4.62	11.36		41.26
	(+0.42)	(+0.02)	(+0.05)	(+0.04)	(−0.24)		(−0.29)
p-Bromoiodobenzene	25.47	1.43				28.24	44.86
	25.03	1.40				28.14	45.43
	(−0.44)	(−0.03)				(−0.10)	(+0.57)

a) The upperline: theoretical values, the medium line: experimental values, and the lower line: error. b) The sulfur atom was neglected in the composition of the sample since it could not be determined.

area of Cl^- in an ion chromatogram and the atomic ratio of H to Cl in an organic chlorine compound, was plotted in Fig. 4. It was found to give a straight line regardless of the Cl content of the compound. The slope(a) of the straight line in Fig. 4 is shown by Eq.1.

$$a = \left(\frac{\mathrm{H}}{\mathrm{Cl}}\right) \times \frac{A(\mathrm{Cl}^-)}{A(\mathrm{H_2S})} = \text{const.} \tag{1}$$

Equation 1 is rewritten by Eq. 2.

$$\frac{2}{a} = \left(\frac{\mathrm{Cl}}{\mathrm{H}}\right) \times \frac{2A(\mathrm{H_2S})}{A(\mathrm{Cl}^-)} = \text{const.} \tag{2}$$

Equation 2 is also given by Eq. 3 for all halogen atoms.

$$\frac{2}{a} = \left(\frac{\mathrm{H}}{\mathrm{X}}\right) \times \frac{2A(\mathrm{H_2S})}{A(\mathrm{X}^-)} = \text{const.} \tag{3}$$

The form of the $(\mathrm{H/X}) \times 2A(\mathrm{H_2S})/A(\mathrm{X}^-)$ in Eq. 3 is the same as that of the correction factor[1] which was used for the determination of the atomic ratio between C, H, O, and N. Therefore, the value of Eq. 3 can be replaced by $K(\mathrm{X}^-)$ which is used for the determination of the atomic ratio between C, H, O, N, and X. The values of $K(\mathrm{X}^-)$ were obtained by analyzing each standard sample (Table 4). They were consistent with a definite value of Eq. 3. Thus the atomic ratio between C, H, O, N, Cl, Br, and I is obtained by Eq. 4.

$$\alpha(\mathrm{wt\%}) = \frac{\sum M(\gamma)K(\gamma)A(\gamma)}{\sum M'(\beta)K(\beta)A(\beta)} \times 100 \tag{4}$$

where α: C, H, O, N, Cl, Br, and I, β: the product obtained by the present method, γ: the product containing an element α, $M'(\beta)$: the value obtained by subtracting the amount of S from the formula weight of β, $M(\gamma)$: the formula weight of α in γ, $K(\gamma)$: correction factor of γ, and $A(\gamma)$: peak area of γ.

Determination of the Atomic Ratio between C, H, O, N, and X in an Organic Halogen Compound. Various organic halogen compounds were analyzed by the present method and the atomic ratio between C, H, O, N, and X was calculated by introducing both chromatographic data to Eq. 4 (Table 5). It can be seen from Table 5 that the atomic ratio between C, H, O, N, and X is obtained satisfactorily by the present method in which only one sample is used.

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