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Pyrolytic Sulfurization Gas Chromatography. VII. The Simultaneous Determination of the Atomic Ratio between C, H, O, and N in a Halo-organic Compound

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The halide produced from a halo-organic compound interferes with the simultaneous determination of the atomic ratio between C, H, O, and N in the compound by the pyrolytic sulfurization gas chromatography, but the interference can be eliminated by allowing the pyrolytic sulfurization of the compound to proceed in the presence of the sodium sulfide formed by the reaction between sodium azide and sulfur.

According to pyrolytic sulfurization gas chromatography (PSGC), which was originated by the present authors, the atomic ratio between C, H, O, and N in a usual organic compound,[1,2] a metallo-organic compound,[3] and a polymer[4] has been successfully and simultaneously determined.

The present study has been carried out to confirm whether or not PSGC can be applied to the analysis of a halo-organic compound. The chromatogram of a halo-organic compound obtained by PSGC was found to be different from that of the compound consisting of C, H, O, and N alone; that is, there were extra peaks which more or less overlapped with the peaks based on C, H, O, and N. This makes the application of PSGC to a halo-organic compound impossible. In order to eliminate the interference of halides, there seem to be two procedures; one is based on the fixation of halides in an ampule, and the other, on the fixation of halides after the crushing of the ampule. The former is better than the latter, since the flowing path in a gas chromatograph is made of stainless steel, which is apt to react with halides. Various substances were added to a sample for the fixation of halides in an ampule; the sodium sulfide (Na_2S) produced by the reaction between sodium azide (NaN_3) and sulfur(S) in a quartz tube which was closed at one end was found to be best for the present purpose. By this procedure, no peaks of halides were observed on the chromatogram, and a simultaneous determination of the atomic ratio between C, H, O, and N in a halo-organic compound could be successfully carried out.

Experimental

Apparatus and Reagents. The reagents and apparatus used were the same as those previously reported[3-6] except that NaN_3 of a guaranteed grade was newly used.

Samples. 5,7-Dibromo-8-quinolinol of a guaranteed grade was recrystallized from benzene for use. Bis(5,7-dibromo-8-quinolinolato)copper(II) and tris(5,7-dibromo-8-quinolinolato)iron(III) were prepared in accordance with the gravimetric procedure[7] by the use of purified 5,7-dibromo-8-quinolinol. The other samples were of a reagent grade for elemental analysis.

Procedure. After 6 mg of S and approximately 0.4 mg of NaN_3 had been placed in a quartz tube, one end of which was closed, the inside of the quartz tube was completely filled with helium by passing helium through it at the rate of 100 cm^3/min; after 10 min the fused end of the tube was carefully heated in an electric furnace. This was followed by the formation of Na_2S by means of the reaction between NaN_3 and S in the tube. To the tube, 0.3—0.5 mg of a sample was then added, and the other end of the tube was fused after 10 minutes' passage of helium at the same flow rate as before, followed by the same operation as in the previous paper.

Results and Discussion

Interferences of Halides. Three typical halides were analyzed by the PSGC method; their chromatograms are shown in Fig. 1, in which (a), (b), and (c) correspond to the chromatograms of ammonium chloride (NH_4Cl), ammonium bromide, and ammonium

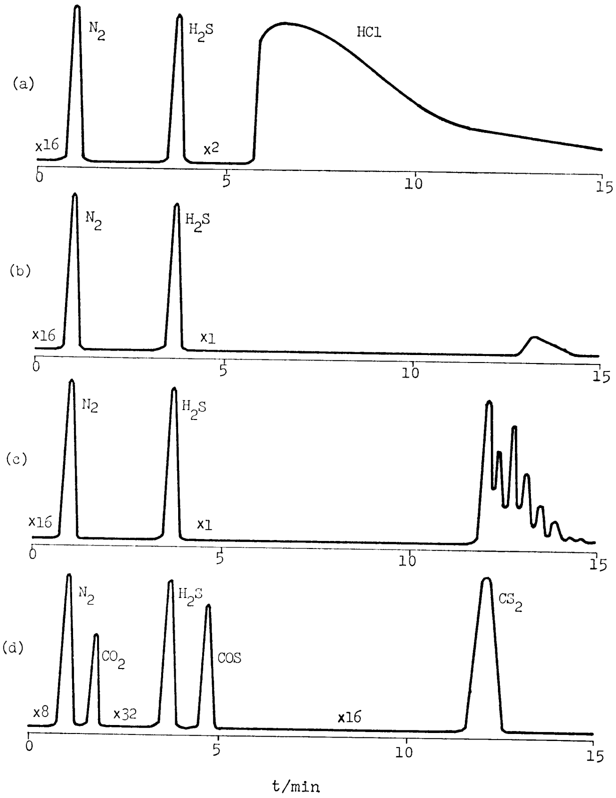

Fig. 1. Typical chromatograms of reaction products between S and ammonium halides by the conventional PSGC method.

(a) NH_4Cl, (b) NH_4Br, (c) NH_4I, (d) glycine as a halogen-free compound.

iodide respectively. As may be seen from Fig. 1, chloride and iodide interfere with the determination of carbon disulfide. Many peaks which appeared after a retention time of approximately 12 min were experimentally confirmed to be due to the compounds formed by the reaction between column packings of the gas chromatograph and iodine or iodide. These results made the application of PSGC to halo-organic compounds impossible. In order to eliminate the interference of halides, a procedure in which halides were fixed in an ampule was adopted, since the flowing path in a gas chromatograph is made of stainless steel, which is apt to react with the halides.

Fixation of Halides. Various substances were added to a sample for the fixation of halides in an ampule, and then the sample was analyzed (Table 1). Since halogen atoms had been completely captured on a silver wire or net in the conventional CH analysis, 1,2,3,4,5,6-hexachlorocyclohexane(γ-BHC) and NH_4Cl were analyzed by the PSGC method in the presence of powdered silver or silver sulfide (Ag_2S), but the peak of hydrogen chloride (HCl) was still observed. Furthermore, when silver chloride was analyzed by the PSGC method in the presence of glycine as a hydrogen source, the peak of HCl was observed. From these results, silver seemed to show a larger affinity for S than chlorine(Cl) and to produce Ag_2S under the present conditions. In these cases, a black solid which might be Ag_2S was observed in an ampule after the pyrolytic sulfurization, differing from the usual yellow contents. Sodium chloride (NaCl) was analyzed similarly as above in the presence of glycine, but no peak of HCl was observed. This suggested that soium (Na) showed a larger affinity for Cl than S under the present experimental conditions. Then γ-BHC and NH_4Cl were analyzed in the presence of the sodium acetate or NaN_3; no peak of HCl was observed, as the authors had expected. γ-BHC was further analyzed in the presence of the acetate of such alkaline earth metals as magnesium(Mg), calcium(Ca), strontium(Sr), and barium(Ba); most of HCl was fixed in all the reaction residues except magnesium acetate ($(CH_3COO)_2Mg$). According to the PSGC method, the acetates of Ca, Sr, and Ba were converted into their sulfides and volatile constituents, while $(CH_3COO)_2Mg$ was converted into its sulfide-oxide mixture and volatile constituents. There might be a correlation between the fixation of HCl and the reaction products obtained from the acetates of alkaline earth metals by the PSGC method. NH_4Cl was sealed into an ampule together with S and NaN_3 to give various atomic ratios of Na to Cl; the evolution of HCl was then investigated (Table 2). As may be seen from Table 2, the sulfide produced by the reaction between S and NaN_3 was found to react with chloride stoichiometrically to produce NaCl. To sum up these results, a basic sulfide was expected to be effective for the fixation of HCl, and so Na_2S was selected and used for the present study. Since Na_2S was very hygroscopic, however, and since its preparation in pure state was also difficult, an attempt was made to produce Na_2S by means of a reaction between S and NaN_3 in a quartz tube on the basis of the facts that NaN_3 decomposed into Na and nitrogen at about 300 °C[8] and Na_2S could be prepared from Na and S.[9,10] The reaction tube containing the Na_2S thus prepared was stable for at least 30 min in contact with air; therefore, the absorption of atmospheric moisture with Na_2S, which might take place during the insertion of the sample, was neglected for the simultaneous determination of the atomic ratio between C, H, O, and N. The present procedure thus established was applied to the three compounds shown in Fig. 1, but no peak based on halides was observed. The present procedure was the same as in the previous papers except for the coexistence of Na_2S, and it could be successfully applied to various halo-organic compounds.

Table 1. Effects of additives on the formation of HCl

Halides	Materials added	HCl
γ-BHC, NH_4Cl	Ag(powder)	+
γ-BHC, NH_4Cl	Ag_2S	+
AgCl	Glycine	+
NaCl	Glycine	−
γ-BHC, NH_4Cl	CH_3COONa	−
γ-BHC, NH_4Cl	NaN_3	−
γ-BHC	$(CH_3COO)_2Mg$	+
γ-BHC	$(CH_3COO)_2Ca$	trace
γ-BHC	$(CH_3COO)_2Sr$	trace
γ-BHC	$(CH_3COO)_2Ba$	trace

Table 2. Effects of the atomic ratio of Cl/Na on the formation of HCl in the NaN_3-NH_4Cl-S system

Atomic ratio		HCl
Na[a]	Cl[b]	
1.0	0.85	−
1.0	1.0	−
1.0	1.2	+

a) NaN_3. b) NH_4Cl.

Analysis of Various Compounds. Various halo-organic compounds, such as chloride, bromide, and iodide, were analyzed by the present procedure (Table 3); metallo-organic compounds containing a halo-organic compound as a ligand were also analyzed (Table 4). It was newly found (*cf.* Table 4) that the atomic ratio between C, H, O, and N in a metallo-organic compound containing both metal and halogen atom could be simultaneously determined.

Analysis of Fluoro-organic compounds. Fluoro-organic compounds were also analyzed by the present procedure (Table 5). As may be seen from Table 5, the result of oxygen was markedly positive. This might be attributed to the formation of water (H_2O) by Eq. 1 in which water hydrogen fluoride (HF) was made to react with the internal surface of a quartz tube, and to the subsequent conversion of H_2O into oxygen-containing compounds:

$$4HF + SiO_2 \longrightarrow SiF_4 + 2H_2O. \quad (1)$$

TABLE 3. ANALYTICAL RESULTS OF HALO-ORGANIC COMPOUNDS

Sample[a)]	C			H			O			N		
	wt%			wt%			wt%			wt%		
	Theor.	Found	Error	Theor.	Found	Error	Theor.	Found	Error	Theor.	Found	Error
1,2,3,4,5,6-Hexachlorocyclohexane $C_6H_6Cl_6$	92.26	92.52	+0.26	7.74	7.48	−0.26						
p-Chlorobenzoic acid C_7H_5Cl	69.42	69.30	−0.12	4.16	4.23	+0.07	26.42	26·46	+0.04			
S-Benzylthiouronium chloride $C_8H_{11}N_2ClS$	71.08	71.15	+0.07	8.20	8.06	−0.14	20.72	20.79	+0.07			
1-Chloro-2,4-dinitrobenzene $C_6H_3O_4N_2Cl$	43.13	43.19	+0.06	1.81	1.83	+0.02	38.30	38.32	+0.02	16.76	16.66	−0.10
1,2,3,4,5,6-Hexabromocyclohexane $C_6H_6Br_6$	92.26	92.33	+0.07	7.74	7.67	−0.07						
N-(α-Bromoisovaleryl)urea $C_6H_{11}O_2N_2Br$	50.34	50.66	+0.32	7.74	7.55	−0.19	22.34	22.43	+0.09	19.57	19.36	−0.21
p-Bromoacetanilide C_8H_8ONBr	71.63	71.61	−0.02	6.02	5.99	−0.03	11.92	11.77	−0.15	10.43	10.63	+0.20
o-Iodobenzoic acid $C_7H_5O_2I$	69.42	69.54	+0.12	4.16	4.11	−0.05	26.42	26.35	−0.07			

a) Halogen atoms were neglected in the calculation of the compositions of halo-organic compounds, since they could not be determined.

TABLE 4. ANALYTICAL RESULTS OF METALLO-ORGANIC COMPOUNDS CONTAINING HALOGEN ATOMS

Sample[a)]	C			H			O			N		
	wt%			wt%			wt%			wt%		
	Theor.	Found	Error	Theor.	Found	Error	Theor.	Found	Error	Theor.	Found	Error
5,7-Dibromo-8-quinolinol $C_9H_5ONBr_2$	75.53	75.47	−0.06	3.51	3.59	+0.08	11.18	11.46	+0.28	9.78	9.48	−0.30
Bis(5,7-dibromo-8-quinolinolato)copper(II) $Cu(C_9H_4ONBr_2)_2$	76.04	76.13	+0.09	2.84	2.79	−0.05	11.26	11.41	+0.15	9.86	9.66	−0.20
Tris(5,7-dibromo-8-quinolinolinolato)iron(III) $Fe(C_9H_4ONBr_2)_2$	76.04	75.85	−0.19	2.84	2.74	−0.10	11.26	11.52	+0.26	9.86	9.89	+0.03

a) Metal atoms and halogen atoms were neglected in the calculation of the compositions of metallo-organic compounds, since they could not be determined.

TABLE 5. ANALYTICAL RESULTS OF FLUORO-ORGANIC COMPOUNDS

Sample[a)]	C			H			O			N		
	wt%			wt%			wt%			wt%		
	Theor.	Found	Error	Theor.	Found	Error	Theor.	Found	Error	Theor.	Found	Error
Fluoroacetamide C_2H_4ONF	41.37	39.04	−2.33	6.94	6.76	−0.18	27.56	30.91	+3.35	24.13	23.31	−0.82
Fluorobenzoic acid $C_7H_5O_2F$	69.42	67.21	−2.21	4.16	4.13	−0.03	26.42	28.65	+2.23			

a) The fluorine atom was neglected in the calculation of the compositions of fluoro-organic compounds, since it could not be determined.

Two experiments were further carried out; in one each ampule contained sodium fluoride (NaF) and S, while in the other each ampule contained NaF, S, and hydrogen. Gaseous oxygen did not evolve in the former, while it did in the latter. It is clear from these results that oxygen is not evolved until HF is produced in an ampule.

According to the present procedure, all the halogen atoms liberated from a halide sample were quantitatively captured in the reaction residues. This suggests a possibility of the simultaneous determination of the atomic ratio between C, H, O, N, and halogen atoms by the subsequent analysis of halogen atoms in the reaction residues.

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