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Functional Group Analysis by Gas Chromatography. IV.[1] Pyrolytic Reaction of Carboxylic Acids in Sulfur Vapor

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This paper deals with a quantitative gas chromatographic analysis of the product evolved by the pyrolytic reaction between carboxylic acid and sulfur vapor. About 10 mg of carboxylic acid was mixed with 2—3 g sulfur and made to react at 1000—1100°C for 10min. The gaseous product was taken in a gas sampler and subjected to gas chromatography. Carbon dioxide was produced from the carboxyl group, carbon disulfide from carbon, hydrogen sulfide from hydrogen and nitrogen molecule from nitrogen. The peak area ratios of carbon disulfide and hydrogen sulfide to carbon dioxide were found in the gas chromatogram with glycine as a standard substance, and the other carboxylic acids were analyzed on the basis of the relation between the peak area ratio and the chemical composition of glycine. Aliphatic and aromatic carboxylic acids gave satisfactory resuls by this method, but not pyridine carboxylic acid. Weighing a definite amount of sample is not needed in this method. Information concerning the chemical composition as well as the functional group of a carboxylic acid can be obtained.

Studies have been carried out synthetically and kinetically pertaining to the reaction between sulfur and organic compounds, especially aliphatic hydrocarbons in a gaseous phase.[2-7] However, none of them has been applied to the analysis of an organic compound.

In a conventional elementary analysis, the sample is subjected to combustion in an oxygen stream and converted into water and carbon dioxide, the water being determined gas-chromatographically with difficulty. Though the method is effective for knowing the chemical composition of the sample, it does not offer

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[1] Part III in this series, T. Hara and S. Ito, This Bulletin, **43**, 3320 (1970).

[2] W. A. Bryce and Sir Cyril Hinshelwood, *J. Chem. Soc.*, **1949**, 3379.

[3] W. J. Thomas and R. F. Strickland-Constable, *Trans. Faraday Soc.*, **53**, 972 (1957).

[4] W. J. Thomas and B. John, *Trans. Inst. Chem. Eng.*, **45**, T119 (1967).

[5] C. M. Thacker and E. Miller, *Ind. Eng. Chem.*, **36**, 182 (1944).

[6] H. O. Folkins, E. Miller, and H. Henning, *ibid.*, **42**, 2202 (1950).

[7] G. W. Nabor and J. M. Smith, *ibid.*, **45**, 1272 (1953).

any information about the functional group. We proposed a new method,[1] in which organic compounds were subjected to pyrolysis in sulfur vapor and the reaction products were analyzed gas-chromatographically. We could determine the chemical composition as well as the functional group.

We investigated the pyrolysis of carboxylic acids in sulfur vapor, in which the reaction products such as hydrogen sulfide, carbon dioxide and carbon disulfide are determined by means of gas chromatography. Since the carboxyl group is quantitatively converted into carbon dioxide, the reaction products other than carbon dioxide are represented on the basis of the amount of carbon dioxide.

Experimental

Reagents. Since commercial crystalline sulfur (analytical grade) contains carbon disulfide, it was dried at 90°C for 24 hr, pulverized and dried again. The other reagents were either of analytical grade, or purified. Helium was of commercial grade.

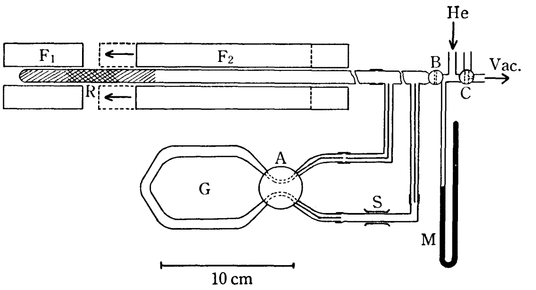

Fig. 1. Apparatus.
F_1,F_2: Electric furnace, G: Gas sampler,
S: Stroke pump, M: Manometer,
R: Reaction tube

Procedure. Two to three grams of powdered sulfur was divided into three portions, the first being charged into a 10 mm diam. × 400 mm quartz tube R with a closed end (Fig. 1). The second is mixed with about 10 mg of sample and charged into the tube, followed by the third portion. The tube was connected to the circulating system with rubber and evacuated through the cocks B and C, followed by replacement of air by helium.

The electric furnaces F_1 and F_2 were held at 750—800°C and 1000—1100°C, respectively. F_2 was placed at a certain position. After three minutes F_1 was placed at another position. F_2 is gradually moved. After completion of the reaction, cock A was closed and the gas sampler separated from the system, followed by gas chromatographic determination of the reaction products.

The reaction temperature was calibrated by a model experiment and maintained within a definite range.

The gas chromatogram was obtained with a Yanagimoto GCG-5DH gas chromatograph under the following conditions: A 2 m stainless steel column was charged with silica gel (60—80 mesh), and held at 100°C. Helium was flowed at the rate of 40 m*l* He/min, and the separated substances were detected with a thermal conductivity detector. The peak area in the gas chromatogram was approximated by the half-width method.

Results and Discussion

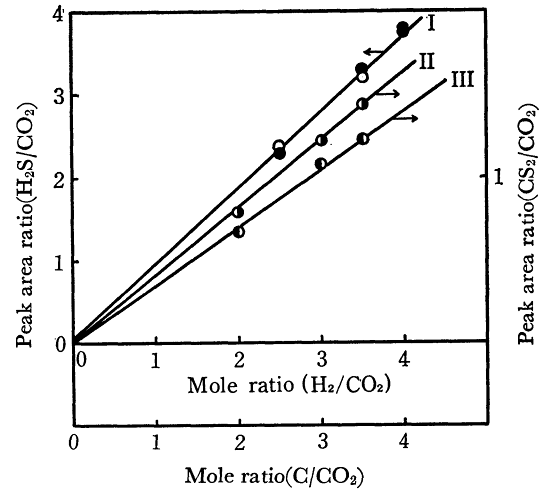

Fig. 2. Relationship between peak area ratios and mole ratios
I: H_2S, II, III: CS_2
○, ◐: 800—850°C, ●, ◑: 1000—1100°C

Effect of Reaction Temperature. In order to examine the effect of reaction temperature on the products, a dibasic aliphatic acid was treated at 800—850°C and 1000—1100°C, and the mole ratios of hydrogen sulfide or carbon disulfide to carbon dioxide were estimated. The results are shown in Fig. 2. The abscissa represents the theoretical mole ratios of hydrogen or carbon to the carbon dioxide based on the -COO- in the carboxylic acid, and the ordinate represents the experimental peak area ratios of hydrogen sulfide or carbon disulfide to carbon dioxide. The amount of carbon disulfide increased at higher temperature while that of hydrogen sulfide was independent of the reaction temperature. Though the amount of carbon disulfide was expected to increase with the rise of temperature, the reaction temperature was kept at 1000—1100°C since hydrogen sulfide had been reported to decompose at temperatures higher than 1000°C in accordance with the following reaction[8]:

$$2H_2S \longrightarrow 2H_2 + S_2$$

Hydrogen sulfide was also produced by the reaction between hydrogen and sulfur at 1000—1100°C. Decomposition of hydrogen sulfide at the same temperature thus seems to be negligibly small in the presence of an excess sulfur. This is supported by the equilibrium constant for the reaction $H_2+{}^1/_2\,S_2 \rightleftharpoons H_2S$, in which $K=P(H_2S)/P(H_2)\times P(S_2)^{1/2}$, and the values of log K are 1.305 at 1218°K and 0.964 at 1338°K.[9]

It is evident that the amount of hydrogen sulfide and carbon disulfide are proportional to the number of hydrogen and carbon atoms in the compounds such as adipic, suberic and azelaic acids.

Effect of Catalyst. Catalysts such as alumina,[5]

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[8] A. J. Owen, K. W. Sykes, and D. J. D. Thomas, *Trans. Faraday Soc.*, **49**, 1207 (1953).

[9] "International Critical Tables," Vol. 7, ed. by E. D. Washburn, Mcgraw-Hill Book Co., Inc., New York and London (1930), p. 237.

silica gel,[5,6] and vanadium pentoxide[3,7] used for the reaction between hydrocarbon and sulfur, were applied to the present reaction. However, the amount of hydrogen sulfide and carbon disulfide evolved did not change so markedly and sulfur dioxide was produced by the reaction between the oxygen in the catalysts and sulfur vapor. These catalysts are not suitable for the determination of the compound containing sulfonic- and nitro-groups since they were converted into sulfur dioxide.[1]

Effect of Stainless Steel Column. The reaction between hydrogen sulfide and stainless steel tube was examined. However, no reaction was confirmed under the conditions in the present procedure.[10]

Determination of Factors by Glycine. The factors for determination of each components were calculated by the equation $E/CO_2 = F(A(E)/A(\mathrm{CO_2}))$, where E: mole number of a particular element in glycine, CO_2: mole number of carbon dioxide in glycine, $A(E)$: peak area of the compound containing a particular element in glycine, $A(\mathrm{CO_2})$: peak area of carbon dioxide in glycine, F: factor.

Assuming the factor of carbon dioxide $F(\mathrm{CO_2}) = 1$, the factors for nitrogen, hydrogen, and carbon are $F(\mathrm{N_2}) = 1.56$, $F(\mathrm{H_2}) = 1.04$ and $F(\mathrm{C}) = 2.97$. The chemical composition of nitrogen, hydrogen, carbon and carboxyl group as carbon dioxide is easily determined by multiplying $A(E)/A(\mathrm{CO_2})$ by F.

Analysis of Aliphatic Carboxylic Acids. The monobasic acids which boil at lower temperature were used as their sodium salts. No carbon dioxide was captured by sodium salt. *n*-Caproic and *n*-caprylic acids were charged in a glass capillary and analyzed. Table 1 shows the results obtained.

Analysis of Amino Acids. Though L-cysteine and L-cystine contain sulfur as components, the sulfur content cannot be estimated by the present method, which is one disadvantage. However, the sulfur content in a sulfonic group is determined as sulfur dioxide. Both L-cysteine and L-lysine were subjected to analysis as their hydrochlorides, but no effect of hydrochloride was found (Table 2).

Table 1. Analytical results of aliphatic carboxylic acids

Compound	Formula	
	Theoretical	Found
Sodium formate	HCO_2Na	$H_{1.0}CO_2$
Sodium acetate	CH_3CO_2Na	$C_{1.0}H_{3.3}CO_2$
Sodium propionate	$C_2H_5CO_2Na$	$C_{2.2}H_{5.3}CO_2$
Sodium butyrate	$C_3H_7CO_2Na$	$C_{2.9}H_{7.1}CO_2$
n-Caproic acid	$C_5H_{12}CO_2$	$C_{5.2}H_{12.3}CO_2$
n-Caprylic acid	$C_7H_{16}CO_2$	$C_{7.4}H_{16.9}CO_2$
Oxalic acid	$H_2(CO_2)_2(HCO_2)$	$C_{1.0}CO_2$
Adipic acid	$C_4H_{10}(CO_2)_2$ $(C_2H_5CO_2)$	$C_{1.8}H_{4.7}CO_2$
Pimelic acid	$C_5H_{12}(CO_2)_2$ $(C_{2.5}H_6CO_2)$	$C_{2.6}H_{5.7}CO_2$
Suberic acid	$C_6H_{14}(CO_2)_2$ $(C_3H_7CO_2)$	$C_{2.9}H_{6.8}CO_2$
Azelaic acid	$C_7H_{16}(CO_2)_2$ $(C_{3.5}H_8CO_2)$	$C_{3.4}H_{7.7}CO_2$
Fumaric acid	$C_2H_4(CO_2)_2$ (CH_2CO_2)	$C_{1.2}H_{2.1}CO_2$

Table 2. Analytical results of amino acids

Compound	Formula	
	Theoretical	Found
L-Alanine	$NC_2H_7CO_2$	$N_{0.8}C_{1.8}H_{6.9}CO_2$
L-Aspartic acid	$NC_2H_7(CO_2)_2$ $(N_{0.5}CH_{3.5}CO_2)$	$N_{0.6}C_{1.3}H_{3.5}CO_2$
L-Glutamic acid	$NC_3H_9(CO_2)_2$ $(N_{0.5}C_{1.5}H_{4.5}CO_2)$	$N_{0.5}C_{1.7}H_{4.6}CO_2$
L-Valine	$NC_4H_{11}CO_2$	$N_{1.2}C_{4.4}H_{11.4}CO_2$
L-Isoleucine	$NC_5H_{13}CO_2$	$N_{1.1}C_{5.4}H_{12.7}CO_2$
L-Cystine	$N_2C_4H_{12}S_2(CO_2)_2$ $(NC_2H_6SCO_2)$	$N_{0.9}C_{1.8}H_{6.3}CO_2$
L-Cysteine-HCl	$NC_2H_7SCO_2 \cdot HCl$	$N_{1.0}C_{1.8}H_{6.9}CO_2$
L-Lysine-HCl	$N_2C_5H_{14}CO_2 \cdot HCl$	$N_{1.8}C_{5.1}H_{14.3}CO_2$
L-Phenylalanine	$NC_8H_{11}CO_2$	$N_{0.8}C_{7.8}H_{10.9}CO_2$
L-Leucine	$NC_5H_{13}CO_2$	$N_{1.1}C_{5.3}H_{12.7}CO_2$

Analysis of Aromatic Carboxylic Acids. In the pyrolytic reaction of aromatic carboxylic acid at 800—850°C, the amount of carbon disulfide evolved was less than that in an aliphatic carboxylic acid. The same factors as for an aliphatic carboxylic acid could, however, be applied to the pyrolytic reaction of an aromatic carboxylic acid at 1000—1100°C (Table 3). This can be attributed to the fact that the carbon-carbon bond energy in a benzene ring is larger than that in an aliphatic compound. Pyridinecarboxylic acid alone did not give a satisfactory result, and no nitrogen being found in a gaseous product. It seems that the pyridine ring is still stable at the reaction temperature or converted into a nonvolatile substance, but this has not been confirmed. By this method we cannot estimate the absolute number of carboxylic group.

Table 3. Analytical results of aromatic carboxylic acids

Compound	Formula	
	Theroetical	Found
Benzoic acid	$C_6H_6CO_2$	$C_{6.3}H_{6.1}CO_2$
p-*t*-Butylbenzoic acid	$C_{10}H_{14}CO_2$	$C_{9.9}H_{14.3}CO_2$
o-Toluic acid	$C_7H_8CO_2$	$C_{6.9}H_{7.7}CO_2$
m-Toluic acid	$C_7H_8CO_2$	$C_{6.8}H_{8.2}CO_2$
p-Toluic acid	$C_7H_8CO_2$	$C_{7.1}H_{8.2}CO_2$
Terephthalic acid	$C_6H_6(CO_2)_2$ $(C_3H_3CO_2)$	$C_{2.9}H_{2.8}CO_2$

Information on the chemical composition as well as functional group of a compound is obtained by this method using an arbitrary amount of sample. The method can be applied to various compounds such as organic compounds or metal complexes.

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10) S. Ito and T. Hara, *Nippon Kagaku Zasshi*, **90**, 1027 (1969).