Functional Group Analysis by Gas Chromatography. III.[1] Pyrolysis of Organic Compounds in Sulfur Vapor

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Many papers have been published on the reactions between gaseous sulfur and organic compounds.[2] However, they have never been utilized in analytical chemistry. This paper deals with the pyrolysis of organic compounds in sulfur vapor, with special reference to the relationship between the pyrolytic products and functional groups.

Two grams of sulfur was placed in a quartz tube 10 mm dia. × 180 mm (Fig. 1) and melted on the tube wall under helium atmosphere. Either a glass boat or a capillary tube containing 10—30 mg solid or liquid sample was inserted into the reaction tube. The tube was then filled with helium, and heated at 850—880°C by means of a movable electric furnace. The time required for the reaction was about 10 min. The stroke pump was then driven and the sample was gas-chromatogramed under the following conditions: column 2 m, charged with silica gel (60—80 mesh); column temp. 100°C; and carrier gas He, 40 ml/min.

The results are shown in Table 1, and a typical pyrogram of sulfanilic acid in Fig. 2.

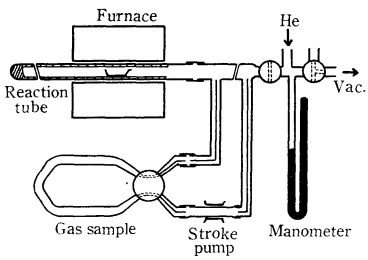

Fig. 1. Apparatus.

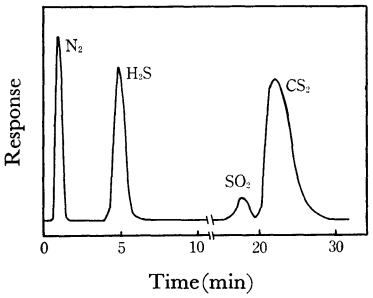

Fig. 2. Pyrogram of sulfanilic acid.

TABLE 1. RELATIONSHIP BETWEEN THE TYPE OF COMPOUND AND PYROLYTIC PRODUCTS

Type of compounds	Compounds	Products found	CO/CO_2 mol ratio
R–COOH	Stearic-, Fumaric-, Cinnamic- and Adipic-acids, Potassium acetate	CO_2 H_2S	
Ar–COOH	Benzoic- and Terephthalic-acids	CS_2	
R–CO–R′	Acetylacetone		>1
R(Ar)–CO–R′	Acetophenone, Benzophenone		<1
(Ring C)=O	Cyclohexanone		<1
Ar–CHO	Benzaldehyde	CO	>1
R(Ar)–O–Ar	Anisol, Diphenyl ether	CO_2	>1
R–COOR′	Ethyl acetate, *n*-Butyl acetate	H_2S	<1
Ar–COOR	Methyl benzoate, Dimethyl terephthalate	CS_2	<1
R–OH	Ethylene glycol, Diethylene glycol, Benzyl alcohol		>1
Ar–OH	Phenol, Hydroquinone, Pyrogallol		<1
Ar–NO_2	Nitrobenzene, 2,4-Dinitrophenylhydrazine	N_2, H_2S, SO_2, CS_2	
R(Ar)–NH_2	Hexamethylenediamine, *o*-, *p*-Phenylenediamines	N_2, H_2S, CS_2	
R(Ar)–CN	Adiponitrile, Phthalonitrile	N_2, H_2S, CS_2	
Ar–SO_3H	Sulfanilic-, Sulfosalicylic-, *m*-Sulfobenzoic- and *p*-Toluenesulfonic acids	(N_2, CO, CO_2), H_2S, SO_2, CS_2	

1) Part II: S. Ito, S. Aikawa and T. Hara, *Nippon Kagaku Zasshi*, **91**, 251 (1970).

2) For example: W. J. Thomas and R. F. Strickland-Constable, *Trans. Faraday Soc.*, **53**, 972 (1957); W. A. Bryce and Sir Cyril Hinschelwood, *J. Chem. Soc.*, **1949**, 3379; C. M. Thacker and E. Miller, *Ind. Eng. Chem.*, **36**, 182 (1944); H. O. Folkins, E. Miller and H. Henning, *ibid.*, **42**, 2202 (1950); G. W. Nabor and J. M. Smith, *ibid.*, **45**, 1272 (1953).