*The Quantitative Determinations of High-boiling Divalent Organo Sulfur Compounds by Copper**

—Determinations of Divalent Sulfur Compounds Formed in the Reaction between Benzene and Sulfur—

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Determinations of aromatic mercaptans, sulfides and disulfides dissolved in hydrocarbon are of considerable importance both in industrial and fundamental investigations. Separation of these high-boiling aromatic sulfur compounds into individual components[1,2] is usually difficult because of the similar chemical behaviors toward many reagents. Especially analysis is more difficult when sulfur is present in samples that are to be distilled.

Heavy metals, such as copper, silver and mercury[3-6], are known to form complexes with divalent sulfur compounds and could be used for the analysis of these sulfur compounds. Such a procedure would have an advantage of great rapidity and simplicity in handling at room temperature over other methods. In this investigation, we have chosen metallic copper and studied in detail the behaviors of copper metal toward various divalent sulfur groups and the scope of application of this procedure for the analysis of various divalent sulfur compounds.

Preparation of spongy active copper powder has been reported by Blumer[7]. Actually, we found that we could make two kinds of copper powders, i. e., red-brown and black copper powders depending upon two different procedures we used. These two different copper powders showed different affinities toward various divalent sulfur compounds. Therefore, these different affinities could be utilized for the separation of divalent sulfur compounds. Divalent sulfur compounds used for this work were benzenethiol, diphenyl sulfide, diphenyl disulfide and thianthrene, which are considered to be present in the products mixture of the reaction between benzene and sulfur. Our results indicate that elemental sulfur and benzenethiol can be eliminated from benzene solution of divalent sulfur compounds by precipitation with red-copper, whereas diphenyl sulfide, disulfide, and thianthrene remained in the solution. When the remaining solution was treated with black copper, the disulfide was found to be eliminated leaving other components in the solution.

Experimental

Preparation of Spongy Active Copper Powder. — *Red-brown Copper*.—Copper sulfate, 45 g., was dissolved into 500 ml. of distilled water containing 50 ml. of 2 N hydrochloric acid and slowly stirred. Fifteen grams of thick slurry zinc was added to this solution at once. Stirring was continued until copper which precipitate turns from black to red-brown color. This copper was washed with distilled water, which was replaced with acetone and then with ether. Red-brown copper was kept in vacuum in dried condition. Completely dried copper

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powder are quite stable in air. But in the presence of even a trace amount of water, copper reacts with oxygen and carbon dioxide in air to form black copper oxide and green $CuCO_3Cu(OH)_2$.

Black Copper.—When about 20 g. of zinc was added to the copper sulfate solution at several time intervals and the mixture was continued to stir, black colored copper precipitated. It was washed with distilled water and was kept in cold.

Preparation of Copper Column.—In this work, a column with bed volume of 20 ml. of copper powder in a glass tube having the diameter of 2 cm. and length of 25 cm. was used. The size of the column could be adjusted depending on the amounts of sulfur compounds. The copper column was soaked with benzene before a benzene solution containing sulfur compounds were passed through.

Preparation of Standard Sulfur Compounds.—Benzenethiol was purchased from Maruwaka Kagaku, Osaka, and diphenyl sulfide was K and K Lab. Inc., Long Island, N. Y., respectively, and both were used after careful distillations. Diphenyl disulfide was prepared by oxidizing benzenethiol with hydrogen peroxide and recrystallized from ethanol.

Results

The divalent sulfur compounds in benzene were characterized by measuring the intensities of ultraviolet absorption at 280 mμ against benzene blank. Benzenethiol, diphenyl disulfide, diphenyl sulfide, thianthrene, thiophene and elemental sulfur, all have the absorption at around 280 mμ. At this absorption spectra, Beer's law was obeyed at concentration around 5×10^{-5} mol./l. for diphenyl disulfide and thianthrene, 2×10^{-5} mol./l. for diphenyl sulfide, 2×10^{-4} mol./l. for benzenethiol and 0.2 mol./l. for thiophene. Molar extinction coefficients of these compounds at 280 mμ was shown in Table I.

TABLE I. MOLAR EXTINCTION COEFFICIENTS OF ORGANO SULFUR COMPOUNDS

Compound	Molar extinction coefficient
Benzenethiol	593
Diphenyl disulfide	2500
Diphenyl sulfide	5700
Thianthrene	2400
Thiophene	0.79

Benzene solution containing benzenethiol or diphenyl disulfide was slowly passed through the red-brown copper column. By this procedure, benzenethiol was removed as can be observed from Table II, but diphenyl disulfide was not effected at room temperature. Benzenethiol apparently reacted with copper to form cuprous phenyl mercaptide, which has yellow

$$C_6H_5SH + Cu \rightarrow Cu_2(C_6H_5S)_2$$

brown color and is not soluble in benzene, water, dilute hydrochloric acid or in ammonia. These chemical properties of this compound suggest a formation of cuprous mercaptide[8].

TABLE II. REMOVAL OF BENZENETHIOL FROM BENZENE

Initial amount of thiol mM	Residual thiol in elute mM
0.80	0.09
1.06	0.14
2.11	0.15

Meanwhile diphenyl disulfide did not form any compound with copper in this condition. Therefore, when both the mercaptan and the disulfide are present in the solution, at first the total absorbancy of the solution at 280 mμ was measured, and then the solution was passed through the red-brown copper column and the absorbancy of the filtrate was measured again. The absorbancy of the filtrate corresponds to the amount of the disulfide. The amount of benzenethiol can be calculated by subtracting the absorbancy of the disulfide from the total absorbancy of the original solution at 280 mμ. Table III shows their analytical data.

TABLE III. DETERMINATION OF BENZENETHIOL AND DIPHENYL DISULFIDE IN BENZENE

Initial concn.		Found	
Thiol mM	Disulfide mM	Thiol mM	Disulfide mM
0.56	0.33	0.55	0.34
0.56	0.24	0.57	0.22
0.93	0.42	0.93	0.34
0.93	0.28	0.93	0.26
0.93	0.14	0.91	0.14
1.34	0.42	1.38	0.40
1.34	0.28	1.38	0.28
1.34	0.14	1.22	0.16

Detection of the disulfide and the sulfide in the presence of elemental sulfur in benzene solution was also tried by the same procedure. Elemental sulfur often presented in these organic sulfur compounds is a serious hazzard in the analysis of these sulfur compounds. To remove elemental sulfur from these divalent sulfur compounds, red-brown copper column was used. Elemental sulfur, the disulfide and the sulfide were dissolved in benzene and this solution was passed through the red-brown copper column. By this procedure only elemental sulfur was removed from the original solution.

In order to determine the amount of the sulfide, the filtrate solution was passed once

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[8] F. Feigl, "Chemistry of Specific, Selective and Sensitive Reactions", Elsevier Pub. Co., Amsterdam (1949), p. 326.

TABLE IV. DETERMINATION OF DIPHENYL DISULFIDE AND DIPHENYL SULFIDE IN THE PRESENCE OF SMALL AMOUNTS OF ELEMENTAL SULFUR

Elemental sulfur per 100 ml. of benzene mg.	Taken		Found	
	Sulfide mM	Disulfide mM	Sulfide mM	Disulfide mM
0	0.33	0.21	0.33	0.21
1	0.071	0.32	0.071	0.32
2.5	0.042	0.16	0.047	0.17
	0.063	0.16	0.068	0.17
	0.072	0.34	0.072	0.34
	0.110	0.12	0.091	0.12
5.0	0.042	0.155	0.047	0.17
	0.063	0.16	0.070	0.16
	0.063	0.28	0.053	0.28
	0.0945	0.28	0.110	0.25
	0.126	0.28	0.140	0.26
10.0	0.042	0.31	0.044	0.265
	0.063	0.28	0.073	0.28

more through the black copper column. By this procedure the disulfide was removed, and the filtrate solution contained only the sulfide. The amount of each sulfur compound was determined by ultraviolet absorption at 280 mμ. Analytical results for the determination of their sulfur compounds were shown in Table IV. Agreement was quite satisfactory. The mechanism of the separation of the disulfide by black copper and the disulfide may produce a similar compound which was obtained by the reaction between the mercaptan and red-brown copper.

A benzene solution containing thianthrene was treated through these copper columns to see how these sulfur compounds behave toward active copper. We found that thianthrene was a little effected by these copper columns. Therefore, active copper is not applicable for quantitative separation of diphenyl disulfide and thianthrene. They were determined by the reaction with concentrate sulfuric acid[9].

These results indicated that the affinities of these divalent sulfur compounds toward active copper depends on the nature of sulfur group. Experimentally determined order of affinities of these sulfur compounds to copper are elemental sulfur>benzenethiol>diphenyl disulfide>thianthrene>diphenyl sulfide.

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[9] K. Sugimoto, W. Ando and S. Oae, *Japan Analyst* (*Bunseki Kagaku*), 12, 38 (1963).