[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ARKANSAS]

DETERMINATION OF SULFUR IN LIQUID ORGANIC COMPOUNDS[1]

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For the analysis of solid organic sulfur compounds various methods utilizing the Parr bomb have been developed which leave little to be desired and satisfactorily supplant the Carius method. In the case of compounds which are liquids at room temperature, this can hardly be claimed. Despite the various precautions which may be used the ignition of liquids is apt to be explosive and, in many instances, premature. For the analysis of such compounds another method of oxidation would be desirable.

The writer investigated the Klason method recently reported in a modified form by Leonard,[2] which seemed the simplest and most direct of the many reported methods. The initial intention was to modify the method so as to replace the expensive platinum catalyst by chromel. Chromel functioned about as well as platinum; however, it was soon found that the empty tube gave almost as good results as either chromel or platinum. This led to a modification in which chips of pyrex glass were substituted for the platinum catalyst. With this change the method becomes eminently satisfactory and there is no difficulty in procuring sufficient of the catalyst to insure complete oxidation of the sample.

One advantage of the Carius method is that several tubes may be run at one time. This has been offset by mounting two tubes side by side. Flashing during the analysis has been practically eliminated by the use of air instead of oxygen; it is, therefore, a simple matter to care for these two analyses simultaneously with good results. When the directions given by Leonard for the evaporation of the solution were followed literally high results were obtained. It was necessary to provide for more complete removal of the nitric acid before precipitating the barium sulfate.

Procedure

The illustration given in Leonard's article should be consulted. The bulb (E) contains about 50 cc. of fuming nitric acid.[3] The sample boat (D) is placed 8 cm. from the end of the tube. This boat need only be used with solids and with liquids whose boiling points lie above 200°. Other liquids are weighed in a bulb with a capillary stem about 5 cm. long. At the time of the analysis the tip of the stem is cut off, the bulb at once inserted in the tube and the cork forced home. The nitric acid boat (B) is placed 8 cm. beyond the sample boat. A free space of some 10 cm. is left beyond the nitric acid boat. Forty to 45 cm. of the tube contains fragments of pyrex glass about 1 cm.

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[1] Paper No. 171, Journal Series, University of Arkansas.

[2] Leonard, THIS JOURNAL, **45**, 255 (1923).

[3] The acid may be used for several analyses; it is quite satisfactory as long as it will freely liberate red fumes.

in diameter (made from old combustion tubes). A considerable free space is left above the chips for the passage of the gases. The receiver contains 100 cc. of water. The combustion tube is wrapped with a single layer of wire gauze over the portion containing the glass chips. This portion should be supported at intervals of 8 to 10 cm.[4] When the apparatus is set up in duplicate, both tubes are wrapped within one sheet of screening. A battery of eight Fisher burners is used to heat the tube. It has not been necessary to use oxygen with this apparatus; only air has been used and flashing (very mild) has only taken place in one or two instances with no interruption of the analysis.

At the beginning of an analysis several burners at the distal end of the tube are lighted and the sample placed in the tube. The rest of the burners are then lighted and the tube allowed to fill with brown fumes. With a very volatile sample it may be well to hasten the production of fumes by gently warming the nitric acid boat. The stream of air carrying nitrogen oxides is then passed through the apparatus; about two bubbles per second should pass the receiver. We have found it advantageous to cover the cork between the bulb (E) and the tube with "Vulcan Paste" to avoid any possibility of a leak. It is well to heat the tube near this cork at once to avoid the collection of liquid at this point, an event which may take place with an easily oxidized compound. When the pyrex chips are at red heat and the tube is completely filled with brown fumes, the sample is heated, gently at first, finally with full heat, until all liquid has been driven over and any charred matter has disappeared.

The combustion will require from one and one-half to two and one-half hours, depending upon the weight of the sample and the character of the compound. At the conclusion of a run the chips are removed from the tube and twice boiled in a beaker with small portions of water. The tube is washed a number of times with 10-cc. portions of hot water. The washings and the liquid from the receiver are combined in a 600-cc. beaker and evaporated to a volume of about 10 cc. Twenty-five cc. of concentrated hydrochloric acid is added and the liquid evaporated as before. The treatment with hydrochloric acid and evaporation is repeated, after which water is added and the solution is treated with sodium hydroxide solution until just acid to litmus. It is then

TABLE I

ANALYSIS OF SULFUR COMPOUNDS

Compound	Percentage of sulfur Calcd.	Volumetric		Gravimetric	
Butyl sulfone	17.99	17.97		17.80	
Di-*p*-tolyl sulfone	13.01	12.99	12.83	12.67	13.07
Thiourea (crude)	42.12	...	...	40.95	40.66
				41.06	41.03[a]
Butyl toluenesulfonate	14.06	13.91	13.90	14.17	14.36
Ethyl thioacetate	30.77	30.87	30.32	31.05	
Phenyl isothiocyanate	23.70	23.31	23.69	23.90	
Ethyl thiocyanate	36.78	37.17	36.71	36.71	
Methyl thiocyanate	43.83	44.31	43.82	43.76	
Tolyl isothiocyanate	21.48	21.19	21.42	21.32	
Thiophenol	29.08	28.98		28.46	28.50
Ethyl sulfide	35.55			34.93	35.13

[a] Result by another method. Analyses performed by Mr. J. G. Womack and Mr. R. H. Philbeck. Preliminary analyses by Mr. A. V. Tuller.

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[4] Our tubes were of pyrex glass. When properly supported and wrapped they could be used eight or nine times before it was necessary to reject them. A quartz tube would have a longer life.

filtered, the volume brought to 300 cc., 2 cc. of 3 *N* hydrochloric acid added and the precipitation of barium sulfate carried out in the usual manner.

Much time may be saved if the estimation of sulfate is performed volumetrically. In this case the filtered acid solution is brought to a volume of 200 cc. and handled as directed in a previous paper on this subject.[5]

Results

Table I cites results secured in the analysis of several organic compounds by this method. The first three compounds are solids. They were analyzed to insure that the method would handle compounds known to be difficult of oxidation or because they had been analyzed by other methods and their sulfur content was known.

Summary

The Klason method of oxidation of volatile organic liquids and solids as reported in modified form by Leonard has been altered so as to replace the expensive platinum catalyst with chips of pyrex glass. Air is used in place of oxygen, thus greatly decreasing the possibility of flashing. The method is recommended for the determination of sulfur in organic liquids and in solids for which the Parr method is unsuitable.

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[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

ROTENONE. II. THE DERIVATIVES OF DERRITOL[1]

BY F. B. LAFORGE AND L. E. SMITH

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Catalytic hydrogenation of rotenone results in the formation of two compounds: dihydrorotenone, a neutral substance in which the original double bond is reduced, and an acid product which still contains the double bond. Both compounds on further reduction yield an acid containing four more hydrogen atoms than rotenone. The acid of formula $C_{23}H_{24}O_6$ will be referred to as rotenonic acid and its reduction product as dihydrorotenonic acid.[2]

This peculiar course of the reduction of rotenone leading to an acid product is characteristic not only of rotenone, but of several of its derivatives.

The action of zinc in alkaline solution on rotenone also results in the formation of two compounds: rotenol, in which the carbonyl group is reduced to an alcoholic group, and a yellow phenolic compound, derritol,

[5] Wertheim, THIS JOURNAL, **52**, 1075 (1930).

[1] Presented before the Division of Agricultural and Food Chemistry at the 78th Meeting of the American Chemical Society, Minneapolis, Minnesota, September 9 to 13, 1929.

[2] LaForge and Smith, THIS JOURNAL, **51**, 2574 (1929).