[CONTRIBUTION FROM THE LABORATORY OF GENERAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

REDUCTION REACTIONS WITH CALCIUM HYDRIDE. II. DETERMINATION OF SULFUR IN SULFUR OILS AND RUBBER[1]

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Oxidative methods used at present for the determination of sulfur in sulfur-containing oils and rubber are time-consuming and painstaking. Having obtained satisfactory results by the reductive method for determining the sulfur content of sulfates, using a preliminary heating with calcium hydride, it seemed desirable to apply this method to the sulfur analysis of other substances.

When volatile sulfur-containing compounds are to be dealt with, as in rubbers or oils, we would no longer be able to carry on open heatings with calcium hydride as in a sulfate analysis. The volatile sulfur-containing compound must be mixed with the powdered hydride in a bomb and the whole heated to around 750°. The residue from such heatings should contain all the sulfur as calcium sulfide, which as a water-soluble sulfide may be iodimetrically determined.

Materials.—In order to test this new method as to its applicability in sulfur determinations on oils and rubbers, many samples of varying sulfur content were obtained. Definite sulfur percentages on these oils as determined by oxidative and reductive methods are given in Table I. Eight *sulfur-bearing oils*, used in industry as cutting and lubricating oils, were analyzed.

Ten different rubber samples obtained from rubber companies were also ground to a finely divided state, sampled and analyzed. The variance in the nature of these rubber samples, with results of analyses upon them, are to be noted in Table II.

It was found difficult to prepare finely divided samples of these rubbers such that an intimate mixture could be made with the powdered hydride. Some of the rubbers could be cut into shreds with scissors and then into small cubes. This is laborious and one still does not have the rubber finely divided. The best method was to use an emery wheel, which quite readily ground the rubber into a finely divided condition. This was especially true of the hard and semi-hard rubbers, and on grinding them a suitable powder was obtained which with calcium hydride gives an intimate mixture. The softer rubbers and gums on being ground would yield

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[1] This paper is prepared from the latter part of a dissertation on reduction reactions with calcium hydride, presented by William E. Caldwell in partial fulfilment of the requirements for the degree of Ph.D. The first part was published in THIS JOURNAL, 51, 2936 (1929).

particles which would again agglomerate. An intimate heating mixture was impossible in their case and our later results show that we had a correspondingly low result in sulfur percentage due to incomplete action with the calcium hydride.

Bombs.—Small bombs of about three-fourths of a cubic inch capacity were used. In the course of the work bombs of different design were used in endeavoring to hold all the gas formed within the bomb. The requirements for a bomb for this work are quite stringent. Because the mass within must be heated to about 800°, the bomb must withstand that temperature and a copper gasket must be used. An attempt was made to estimate the pressure that would be reached in the bombs.

Assuming that a 1-g. sample of an oil with an average molecular weight of 224 is taken, and that the gas capacity of the one-half filled bomb is about 10 cc.

224 g. of oil would yield 22,400 cc. of gas at 0° and 760 mm.

1 g. of oil would yield 100 cc. of gas at 0° and 760 mm.

P, 1 atm.; V, 10 cc. air + 100 cc. (potential volume of oil vapor); T, 273°K.; P', x; V', 10 cc.; T', 1073°K.

$$\frac{PV}{T} = \frac{P'V'}{T'}$$

$$P' = 43.2 \text{ atm.}$$

$$43.2 \times 14.7 = 625 \text{ pounds per sq. inch}$$

Considering these assumptions, a pressure of six hundred and twenty-five pounds per square inch may be built up in the bomb. The pressure could be more if cracking of the oil to smaller molecules occurred or if an oil of a smaller average molecular weight were taken. Pressure might also be developed by decomposition of the hydride to calcium and hydrogen vapors. However, the pressure may be considerably less in that much calcium carbide is formed and organic matter thus combined in the solid state.

Accordingly a bomb must be made of materials of such thickness as to withstand these pressures and temperatures. On the other hand, a bomb of as little weight as possible is desired so that heating and cooling may be rapid.

It is admitted that we have not developed a wholly satisfactory bomb for use in this work. Bombs have allowed gas to leak by the gaskets and through the threads. This is considered then to be the source of low results in the determination of sulfur in very volatile oils containing low molecular weight mercaptans, disulfides, etc.

Solutions and Calcium Hydride.—Carefully standardized 0.1 N iodine and sodium thiosulfate solutions were used as in previous work for determining the water-soluble sulfide in the residue after the heating of sulfate compounds with hydride. A calcium hydride powder of less than sixty mesh was used in intimate contact with the oil and rubber in a manner similar to that in the work on insoluble sulfates.

Experimental

Sulfur Content of Oils.—Weighed amounts of the oils are poured into the bombs containing about 7 g. of the powdered calcium hydride. The oil is quite readily mixed with the hydride by means of a small glass rod. A gram or two more of the hydride is pressed into the bomb over the oil–powder mixture. The bomb is tightly sealed and quickly heated to redness in a muffle furnace or over a Méker burner. After the bomb has been at a bright red heat for ten minutes it is allowed to cool. The contents are readily removed from the bomb and placed in a 500-cc. Erlenmeyer flask. The residue is moistened with about 20 cc. of dry alcohol. This is to prevent dusting, which would occur if water were immediately dropped upon the hydride. Water is now slowly added to the moistened fusion mass from a dropping funnel which is above a reflux condenser at the bottom of which is placed the Erlenmeyer flask. After the excess hydride and the carbide formed have been decomposed, additional water is added to make a solution of about 400 cc. It is well to add some ice in place of a portion of the water so that the solutions will be cool for a better end-point in ensuing titrations.

Before iodine titration, the mass is placed in a liter beaker and an excess of concentrated hydrochloric acid added with a minimum of stirring. The large volume of water is necessary to dissolve and hold the hydrogen sulfide obtained on acidifying the calcium sulfide solution.

The resulting hydrogen sulfide solution is titrated for sulfur content with the 0.1 *N* iodine solution, one cubic centimeter of the iodine solution being equal to 0.0016 g. of sulfur.

Sulfur Content of Rubber.—Rubber samples are treated in a manner similar to that for oils except that the powdered rubber is intimately stirred into the finely divided hydride.

Sample weights of the oils and rubbers are taken so that one can expect a 10–50 cc. iodine titration. For substances expected to contain less than 3% sulfur, a sample up to 1.5 g. is taken. For a hard rubber of around 20% sulfur, a 0.25-g. sample should suffice.

Table I gives the results of sulfur analysis on oils by Eschka's oxidative method compared with percentage sulfur as determined by the above outlined reductive method. Samples 1–8 are on cutting and lubricating oils, the sulfur having been incorporated into these products by heat and pressure. The sulfur compounds so formed are not volatile at low temperature.

Three samples of petroleum oil were analyzed both by Eschka's and our methods. Neither method gave check results or indicated the total sulfur in these oils. Such an oil of low sulfur percentage and containing very volatile sulfur compounds must be treated by some digestion and oxidative method.

Table II lists results of sulfur analyses on rubbers by oxidative and reductive methods. Some other rubbers were tried with discouraging results. These rubbers were mainly of a sticky nature such that an intimate mixture of their macerated form could not be made with the powdered calcium hydride.

TABLE I

SULFUR CONTENT OF OILS

Oil no.	S content (Eschka's method), %		S content (CaH_2 method), %			Remarks
1	6.77	6.76	6.80			High sulfur oil. Used 0.7-g. sample.
	7.08	6.55	6.91			Heavy viscous oil
2	2.32		2.46	2.49		Heavy black oil
	2.46		2.50	2.25		
3	4.83		4.63	4.61	4.40	Heavy black oil
	4.79		4.54	4.62	4.63	
			4.82	4.53		
4	1.70		1.78			Animal or vegetable oil. Contains H_2O
	1.74		1.73			
5	0.275		0.33			Light oil, some oleic acid, water, little S
	0.27		0.40			
6	1.97		2.10			Light, somewhat volatile oil
	2.03		2.11			
	2.02					
7	1.4		1.46			A solid, fatty substance
	1.31		1.45			
8	3.77		4.00			Oil not wholly homogeneous. Heavy black oil
	4.00		4.25			
	3.20		3.87			

TABLE II

SULFUR CONTENT OF RUBBERS

Sample no.	Sulfur (oxidative), %		Sulfur (CaH_2 method), %		Remarks
1	22.61		21.40		A very hard black rubber. Powders readily on grinding
	22.50		22.40		
2	1.77		1.9		Soft, but grinds to fluffy powder
3	1.35		1.44		Brown shoe sole
4	1.83		1.83		Black crumbly rubber
5	1.29		1.25		Pink crumbly rubber
6	2.15		2.19		A piece of tire. Hard to macerate
7	2.76		2.63	2.51	Shoe sole or belting
8	2.75		2.68		Black rubber plate
9	1.63	1.58	1.58		Rubber casting
10	29.6		29.3	29.8	Ground fountain pen casing

Miscellaneous Sulfur Determinations.—Two 0.05-g. samples of free sulfur were heated in bombs with 5 g. of calcium hydride. The cooled residue on analysis for water-soluble sulfide gave results corresponding to 0.0512 and 0.0496 g. of sulfur. Thus free sulfur may be determined within a 2% error even on such small samples.

Samples of sodium thiosulfate were similarly treated to determine their sulfur content. Considering the sample to be $Na_2S_2O_3 \cdot 5H_2O$ it would contain 25.8% of sulfur. An average of our analyses showed it to contain 25.34%.

Discussion of Results

It is evident from a consideration of results obtained that the method here presented of determining sulfur in insoluble sulfates may be extended to the determination of sulfur in oils and rubbers when one uses a gas-tight bomb instead of the open crucible. All of the sulfur in the organic material is converted to calcium sulfide when heated to 700° in contact with calcium hydride. The water-soluble sulfide thus formed may be determined by iodimetry. The method lends itself most readily to determinations in rubbers and oils of high sulfur content, and presents itself as a rapid method for the determination of sulfur in this type of material.

Summary

1. Sulfur may be determined in sulfurated oils by fusion of the oils with calcium hydride, followed by an iodine titration on an acidified solution of the fusion residue.
2. A method of determining the percentage of sulfur in some rubbers is presented.
3. By this method it is possible to determine the percentage of sulfur in free sulfur, sodium thiosulfate and similar sulfur-containing compounds.

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COMPOSITION OF THE GUM PRODUCED BY ROOT NODULE BACTERIA

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One of the most striking characteristics of the root nodule bacteria is the gummy or viscous nature of the colonies or streak cultures. The mucinous appearance of the cultures has been reported by many investigators[1] and has been attributed to the formation of dense capsules by the organisms. What function the gum performs in the metabolism of the bacteria or in their relation to the host plant is not known. Grieg-Smith[2] suggests that the gum is used by the plant and built into nitrogenous compounds, while Mazé[3] is of the opinion that the gum itself is the nitrogenous compound supplied the plant by the bacteria. That the latter assumption is

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[1] (a) M. W. Beijerinck, *Bot. Ztg.*, **46**, 754 (1888); (b) G. F. Atkinson, *Bot. Gaz.*, **18**, 157 (1893); (c) L. Hiltner, *Centr. Bakt.*, II Abt., **6**, 273 (1900); (d) M. Dawson, *Phil. Trans. Roy. Soc.*, **B193**, 51 (1900).

[2] R. Grieg-Smith, *Centr. Bakt.*, II Abt., **30**, 552 (1911).

[3] M. Mazé, *Ann. de l' Inst. Pasteur*, **12**, 1 (1898).