Summary

1. A new field of investigation of nitride-carbide tautomerism is outlined.
2. The sodium salt of phenylacetonitrile and that of α-phenylbutyronitrile have been prepared. Their behavior with acid suggests the nitride structures $[(C_6H_5)HC{=}C{=}N^-]Na^+$ and $[(C_6H_5)(C_2H_5)C{=}C{=}N^-]Na^+$ for the two salts.
3. The behavior of the salts in substitution reactions suggests for them carbide structures $[(C_6H_5)(CN)HC^-]Na^+$ and $[(C_6H_5)(C_2H_5)(CN)C^-]Na^+$.
4. The "double behavior" of the salts indicates a tautomeric relationship between the nitride and carbide forms.
5. The salts are considered to be unstable intermediate products in the aldol-like condensation reactions described by E. von Meyer.

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THE USE OF THE CARIUS METHOD FOR THE DETERMINATION OF SULFUR IN THE LESS VOLATILE PETROLEUM OILS[1]

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Largely because of the tedious and difficult technique involved, the Carius method has been shunned in the determination of sulfur in petroleum, although it is the method recognized as standard by most organic analysts. It is inapplicable to low sulfur oils, as the relatively small sample that must be used gives an amount of barium sulfate that is not readily handled. When the greatest accuracy is required in the determination of sulfur in petroleum oils containing 0.5% or more of this element, the Carius method must presumably be used.

To insure complete decomposition of petroleum oils, the procedure usually applied to organic compounds needs some revision with regard to weight of sample, quantity of fuming nitric acid and method of heating. Such changes are also necessary because the percentage of sulfur, even in high sulfur petroleums, is much less than is usually found in the average organic substance. Mabery and Smith[4] noted that certain conditions must be observed if the method is to give accurate results with sulfur containing petroleum oils. Unfortunately they failed to state these conditions fully or to present data from which the accuracy of their statements could be judged.

It is believed, therefore, that the experimental conditions worked out

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[4] Mabery and Smith, *Am. Chem. J.*, **16**, 84 (1894).

by the writers while making many sulfur determinations by the Carius method will prove helpful to others desiring to use the method under similar conditions. The procedure outlined below is not intended to be complete in detail, as a very full account can be found in the excellent book by Gattermann.[5] It attempts only to set forth and emphasize the conditions essential to success with petroleum oils of the less volatile type containing over 0.5% of sulfur.

Method

Weigh accurately a sample of oil of approximately 0.25 g. into a glass tube about 4 inches long and of $^1/_4$-inch bore.. By means of a long stemmed funnel, introduce into a Carius bomb tube[6] 4 cc. of pure fuming nitric acid. Allow the tube containing the sample to slide slowly down into the acid, taking care that there is no contact between oil and acid. Seal the Carius tube in the usual manner[7] and place in the furnace.

Increase the temperature of the furnace gradually, during a period of seven hours, from room temperature to 175°. Cut off the heat. When the tube is thoroughly cool, hold the capillary cautiously in a luminous flame to drive back any liquid which has accumulated there. Then place the extreme end of the capillary in a hot flame to release the pressure. Reseal, replace in the furnace and resume heating. Bring the temperature rapidly to 175° and then increase to 225° gradually during the succeeding seven hours. Stop the heating and release the pressure as before. Again resume heating; bring the temperature quickly to 225° and then increase gradually during the succeeding seven hours to 300°. Release the pressure. The heating is now complete.[8]

Mark with a file the end of the tube bearing the capillary, break the tube and transfer the contents together with the washings to a 400-cc. beaker. The total volume should not be in excess of 250 cc.

Filter through a qualitative paper and wash the filter three times. Place on a hot-plate and evaporate to a volume of 5 to 10 cc.; transfer to a steam-bath for four hours, or longer if necessary, to remove nitric acid.[9]

Add 75 cc. of water and 5 drops of hydrochloric acid (sp. gr., 1.18) and bring to boil. Add 10 cc. of a hot 10% solution of barium chloride drop by drop, with constant stirring. Keep the solution hot for one hour, subsequently allowing it to stand for twelve hours. Filter through an ashless filter paper, ignite and calculate the percentage of sulfur from the weight of the barium sulfate precipitates.[10]

Experimental

Sulfur (flowers) was dissolved in white, sulfur-free[11] medicinal oil to give an oil containing approximately 0.49% of sulfur. A large number

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[5] Gattermann, "The Practical Methods of Organic Chemistry," translated by Schober and Babasinian, The Macmillan Co., New York, **1921**, 3rd American ed.

[6] The type used is made of heavy-walled, soft glass tubing provided with a constriction near the open end; length, 70 cm.; diameter outside, 22 mm.; obtainable from most of the chemical laboratory supply houses.

[7] Ref. 5, p. 63.

[8] The contents of the tube should show no evidence of undecomposed oil or free carbon. The liquid will be clear and dark green to pale green.

[9] Scarcely any signs of liquid will remain in the beaker.

[10] A blank is run by adding 4 cc. of fuming nitric acid to 250 cc. of water and carrying through as a regular determination.

[11] Containing less than 0.01% of sulfur.

of determinations indicated that 0.4 g. of this oil required approximately 4 cc. of fuming nitric acid for its decomposition under the experimental conditions. The use of larger amounts of sample or acid almost invariably led to explosion of the tubes.

In the first set of Carius determinations successfully completed, these proportions of the prepared sulfur oil and acid were used. The heating was conducted as directed in the method except that the heating periods were of four hours' duration. Upon cooling, the contents of the tubes were light green and clear. To all appearance decomposition was complete.

The contents of the respective tubes were washed into 400-cc. beakers, filtered and evaporated to a volume of 75 cc. Precipitation of the sulfate was brought about in the usual manner by addition of a hot 10% solution of barium chloride. After filtering and igniting, the following results were obtained: 0.480, 0.491, 0.522, 0.501 and 0.517% of sulfur; average, 0.502%.

The variation between individual results was considered much too great. It seemed likely that the error resulted from the interference of nitric acid; but even evaporation to a "small volume" before precipitation, as recommended by Treadwell-Hall,[12] did not remove the acid completely enough. Evaporation to small volume (10 cc.) on the hot-plate, followed by heating on the steam-bath until the beakers were practically "dry" led to satisfactory results.

Another set of Carius determinations was made on the prepared sulfur oil, using 0.4 g. of oil, 4 cc. of pure fuming nitric acid and three four-hour periods of heating as outlined above. The washings were evaporated almost to "dryness" as just described, 75 cc. of water was added, then five drops of hydrochloric acid (sp. gr., 1.18) and precipitation brought about as before. The results were as follows: 0.477, 0.481, 0.481, 0.482 and 0.482% of sulfur; average, ±0.481%. These results were considered satisfactory.

The next step involved the use of an oil in which the sulfur (approximately 2.5%) occurred naturally.[13] A set of determinations was made on this oil using a 0.4g. sample, 4 cc. of fuming nitric acid and heating for three four-hour periods. The washings were evaporated to "dryness" on the steam-bath and the following results were obtained: 2.38, 2.40, 2.31, 2.41 and 2.44% of sulfur; average, ±2.39%.

Although the agreement of the individual results was fairly good, it remained to be shown beyond a reasonable doubt that oxidation was complete. Accordingly, a set of determinations was made on the same oil using

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[12] Treadwell-Hall, "Analytical Chemistry," John Wiley and Sons, Inc., New York, Vol. **II**, 6th ed., revised, **1924**, p. 326.

[13] The oil used in this work was extracted from a heavier oil by means of 95% ethyl alcohol. Its properties were: sp. gr. $\frac{37.7°}{15.6°} = 0.948$; viscosity at 37.7° = 2.592 Poises; S = **2.55%**.

only a 0.25g. sample. The use of 4 cc. of fuming nitric acid and three four-hour heating periods was retained. The results were: 2.46, 2.47, 2.41, 2.48, 2.49 and 2.40% of sulfur; average, ±2.45%.

Since this average was materially higher than the previous one (2.39% S) it seemed possible that oxidation was still incomplete. It was impracticable to decrease the weight of sample below 0.25 g. or to increase the volume of fuming nitric acid above 4 cc. The time of heating was accordingly increased. A set of determinations was run, using a 0.25g. sample, 4 cc. of fuming nitric acid and heating for three seven-hour periods, the same temperature intervals as before being retained. The pressure was released at the end of each period. The results were: 2.52, 2.51, 2.55 and 2.50% of sulfur; average, 2.52%. Since this figure showed still an appreciable gain over the preceding one (2.45% S), another set of determinations was made in which the heating was increased to three fifteen-hour periods. The other conditions remained unchanged. The results were: 2.61, 2.54, 2.51, 2.57, 2.59 and 2.50% of sulfur; average, ± 2.55% S. As this figure agrees with the preceding one (2.52% S) within the experimental limits of the method, it was assumed that the three seven-hour heating periods were sufficient to decompose the oil completely.

There appears to be no way of checking the absolute accuracy of this result, as almost nothing is known concerning the sulfur compounds in the lubricating fractions of petroleum. The statement is sometimes found in textbooks that sulfones resist decomposition by fuming nitric acid and when present in Carius sulfur determinations lead to low results. Accordingly, the sulfur in a carefully purified sample of *n*-butyl sulfone was determined by the method outlined above. The results were: 18.16, 18.27, 18.23 and 18.17% of sulfur; average, 18.21%. Calcd. for *n*-butyl sulfone, 17.99. With this sulfone, therefore, there seems to be no difficulty in determining sulfur with a proper degree of accuracy.

Summary

Specific directions are given for use of the Carius method to determine sulfur in the less volatile petroleum oils. Especial care is necessary to effect complete oxidation. Nitric acid is completely removed before the barium sulfate is precipitated.

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