

The bromine water method was found applicable to a naphtha solution of *n*-butyl sulfide which was free from unsaturated hydrocarbons. "Skelly-solve C," essentially normal heptane, boiling range 90 to 100°, of water white color, and sulfur free (Doctor Test), purchased from the Skelly Oil Company, was freed from a small amount of unsaturated hydrocarbons by prolonged agitation with concentrated sulfuric acid; the acid was washed out, and the naphtha steam distilled and dried. Twenty-five cc. of this purified naphtha was added to 25 cc. of a benzene solution of *n*-butyl sulfide containing 0.1000% sulfur. Duplicate analyses by the bromine water method gave results which were 0.2 and 0.4% higher than those obtained in the benzene solution alone.

Summary

1. A method has been devised for the estimation of alkyl sulfides dissolved in benzene.
2. The method is applicable to a naphtha solution free from unsaturated hydrocarbons.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

SOME ANALYTICAL REACTIONS OF ALKYL MERCAPTANS IN BENZENE SOLUTION¹

BY JOHN R. SAMPEY² AND E. EMMET REID³

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It has been customary to estimate mercaptans by an iodimetric method.⁴ In an examination of this method as applied to dilute solutions in benzene, it has been found that the time allowed for the oxidation is an important factor. The present paper describes also a study of two additional methods for the estimation of mercaptans in dilute concentrations in hydrocarbon solvents. One of these methods involves the titration of the hydriodic

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² American Petroleum Institute Research Fellow.

³ Director, Project 28.

⁴ Kimball, Kramer and Reid, *THIS JOURNAL*, **43**, 1199 (1921).

acid formed by the oxidation of the mercaptan with iodine. The second method is based upon the estimation of the hydrochloric acid produced by the action of an aqueous solution of mercuric chloride on the mercaptan.

Estimation of Mercaptans by Iodimetry.—In a study of the time required for the oxidation of mercaptans by iodine a peculiar phenomenon was observed. When exactly 50 cc. of a benzene solution of *n*-butyl mercaptan (0.0500% S) and 50 cc. of an approximately *n*/40 iodine solution were allowed to stand for twenty minutes and then titrated with a standard solution of sodium thiosulfate until the aqueous layer gave no color reaction with starch solution, it was found that less thiosulfate was required than corresponded to complete oxidation of the mercaptan to disulfide; based upon the amount of iodine apparently consumed, the calculation gave 105.9% of mercaptan oxidized. The benzene layer, however, was strongly colored with iodine, and while it was not possible to decolorize it even upon vigorous shaking with a few drops excess of thiosulfate, after several minutes the purple color appeared again in the aqueous layer, with a decrease in the intensity of the iodine color in the benzene layer. The addition of a few drops of thiosulfate solution caused only the aqueous layer to become colorless again, and to remain so for several minutes of shaking. The addition of thiosulfate was continued in small amounts until both the benzene and the aqueous layers were colorless; a calculation from the total thiosulfate consumed in the several titrations gave 99.9% oxidation to the disulfide.

In a second series of experiments an attempt was made to follow more closely the reaction between iodine and mercaptan. The same concentrations of iodine and mercaptan were used, but the titrations with thiosulfate were begun immediately, and continued at stated intervals; just enough thiosulfate was added each time to decolorize the aqueous starch layer after vigorous agitation. The results of one series of titrations are expressed in Table I.

TABLE I
RATE OF OXIDATION OF MERCAPTAN WITH IODINE

Time, min.	Thiosulfate consumed, cc.	Time, min.	Thiosulfate consumed, cc.
0	7.0	30	16.2
5	8.0	40	17.5
10	11.5	60	19.0
15	12.8	80	20.5
20	14.0	1200 (20 hrs.)	24.3

The final titration at the end of twenty hours corresponded to 99.8% oxidation of the mercaptan present. These results suggest the formation of an intermediate addition compound between the iodine and the mercaptan. This problem is being investigated further.

From a purely analytical point of view, however, it was of more impor-

tance to determine the time required for the reaction to go to completion than to follow its course in the early stages. In order to determine the minimum length of time required for the oxidation, the same concentrations of *n*-butyl mercaptan and iodine as used above were permitted to stand for forty minutes before titration; under these conditions the oxidation was 98.8% complete. From a number of analyses on the normal mercaptans from ethyl through nonyl it was found that three hours was long enough for the reaction to go to completion. Several of the secondary mercaptans, however, were discovered to oxidize much slower; for example, 50 cc. of secondary nonyl mercaptan (0.0500% S) was only 91.2% oxidized in three and one-half hours by 50 cc. of *n*/40 iodine solution. Whenever a long-chained secondary mercaptan was present, it was found best to permit twenty-four hours for the oxidation; during this period the solutions were kept in the dark to prevent the formation of iodine from the hydriodic acid produced during the oxidation.

Modification of the Iodine Method.—Two acidimetric processes for the estimation of mercaptans have been studied. The first of these involved the titration of the hydriodic acid formed during the oxidation of the mercaptan in the iodimetric method. In the second method, the hydrochloric acid liberated by the action of mercuric chloride on the mercaptan is estimated. The procedure for the estimation of the hydriodic acid may be described briefly as follows.

Exactly 50 cc. of a benzene solution of the mercaptan is allowed to stand in a glass-stoppered flask with an excess of the iodine solution until the oxidation is complete. The excess iodine is then removed with thiosulfate solution. The aqueous and benzene layers are separated, and the latter is washed with 60 cc. of water in three portions in order to free it from any hydriodic acid. The washings are added to the main aqueous layer, and the hydriodic acid is titrated with *n*/40 sodium hydroxide solution, using brom cresol purple or a purified litmus solution as indicator.

The accuracy of this method is seen in Tables II and III, where the same samples were used for the estimation of the mercaptan by the iodine and the hydriodic acid methods; the sodium hydroxide titration on each sample was performed as soon as the excess standard iodine solution had been titrated with thiosulfate solution, and the benzene layer separated and washed. The hydriodic acid method is not as accurate as the iodine method, but it was developed in the expectation that it would prove useful where the other would not apply, *e. g.*, in the estimation of mercaptans in mixtures containing unsaturated hydrocarbons.

The solutions used in Tables II and III were prepared by weighing out in a small stoppered weighing bottle the calculated amounts of mercaptans to give a liter of the specified concentration. Fifty-cc. portions of these were pipetted into glass-stoppered flasks for the analyses. The samples of the pure mercaptans were prepared by Dr. L. M. Ellis, Jr.⁵

⁵ Ellis and Reid, *THIS JOURNAL*, 54, 1674 (1932).

TABLE II
COMPARISON OF THE IODINE AND HYDRIDIC ACID METHODS FOR THE ESTIMATION OF
MERCAPTANS

Mercaptan	S present, %	Iodine method, %		Hydriodic acid method, %	
		S found	Error	S found	Error
Ethyl	0.0500	0.0498	-0.4	0.0498	-0.4
	.0500	.0499	-0.2	.0500	0.0
Isopropyl	.0500	.0499	-0.2	.0500	0.0
	.0500	.0498	-0.4	.0498	-0.4
<i>n</i> -Butyl	.0500	.0500	0.0	.0502	+0.4
	.0500	.0499	-0.2	.0498	-0.4
<i>Sec.</i> -hexyl	.0500	.0501	+0.2	.0496	-0.8
	.0500	.0502	+0.4	.0497	-0.6
<i>n</i> -Nonyl	.0500 ^a	.0506	+1.3	.0507	+1.4
	.0500 ^a	.0508	+1.6	.0509	+1.8

^a The solution of *n*-nonyl mercaptan was evidently too strong, for both methods gave high results.

TABLE III
ESTIMATION OF VARYING CONCENTRATIONS OF *n*-BUTYL MERCAPTAN

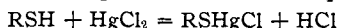
S present, %	Iodine method, %		Hydriodic acid method, %	
	S found	Error	S found	Error
0.2000	0.1998	-0.1	0.2020	+1.0
.2000	.2004	+0.2	.2024	+1.2
.1000	.1004	+0.4	.0989	-1.0
.1000	.1003	+0.3	.1001	+0.1
.0500	.0500	0.0	.0502	+0.4
.0500	.0499	-0.2	.0498	-0.3

Limitations of the Iodine and Hydriodic Acid Methods in the Presence of Naphthas and Unsaturated Hydrocarbons.—No complications were encountered in the determination of mercaptans in naphtha solution ("Skellysolve C") which had been freed from unsaturated hydrocarbons.⁶ In the presence of amylene, however, neither the iodine nor the hydriodic acid method was applicable. An attempt was made to analyze 25 cc. of a benzene solution of *n*-butyl mercaptan (0.1000% S) to which had been added 25 cc. of a 1% amylene solution (in benzene). After this solution had stood for twenty-four hours with 50 cc. of *n*/40 iodine solution, the thiosulfate titration of the excess iodine gave an apparent sulfur content of 0.1077% due to addition of the iodine to the double bond of amylene. From the titration of the hydriodic acid only 0.0992% S was indicated. A duplicate analysis gave 0.1028% S from the iodine titration, and 0.0881% S from the hydriodic acid titration.

Mercuric Chloride Method for the Estimation of Mercaptans.—Mercaptans dissolved in benzene may be estimated rapidly through the use of an aqueous solution of mercuric chloride. Individual mercaptans have often been identified by the melting points of the salts formed from the

⁶ Sampey, Slagle and Reid, THIS JOURNAL, 54, 3401 (1932).

action of an aqueous or alcoholic solution of mercuric chloride upon a naphtha solution of the mercaptan. From the equation for the reaction



it is seen that one mole of acid is liberated for each mole of mercaptan. The method of analysis based upon the titration of the acid may be indicated as follows.

Fifty cc. of a benzene solution of the mercaptan (0.0500% S) is shaken vigorously for three minutes with 25 cc. of a 1% aqueous solution of mercuric chloride; the amount of the mercury salt which precipitates varies with the individual mercaptan; the higher secondary mercaptans give salts which are completely soluble in the 50 cc. of benzene. In the event no precipitation takes place, or only a slight precipitate is formed, the two layers are separated and the hydrochloric acid is washed from the benzene with three 25-cc. portions of water; the acid in the aqueous layer and the washings is titrated with $n/40$ sodium hydroxide, using methyl orange or methyl red as indicator. When a heavy precipitate is formed by the mercuric chloride it is better not to attempt a separation of the two layers, but to add the alkali to the mixture slowly with frequent shakings; methyl orange must be used in this case, for methyl red dissolves in the benzene and becomes orange colored even when there is acid in the aqueous layer; since methyl orange is more soluble in the aqueous layer, and the white precipitate of RSHgCl remains in the benzene layer, the end-point is almost as sharp as when the layers are separated.

Calculations from the preliminary titrations gave results which were low. This was to be expected since both methyl orange and methyl red change color on the acid side. It was necessary to use this type of indicator, however, in order to prevent the formation of $\text{Hg}(\text{OH})_2$. It was found possible to apply a correction factor by standardizing against $n/40$ hydrochloric acid a volume of sodium hydroxide approximately the same as that required in the titration after the mercuric chloride treatment of the mercaptan. The values obtained in the standardization with hydrochloric acid when methyl orange and methyl red were the indicators were 0.4 to 0.5 cc. lower than the results when brom cresol purple and purified litmus were the indicators.

Table IV gives the results of the analyses of benzene solutions of mercaptans.

TABLE IV
MERCURIC CHLORIDE METHOD FOR THE ESTIMATION OF MERCAPTANS

Mercaptan	S present, %	S found, %
Ethyl	0.0500	0.0503
Isopropyl	.0500	.0498
<i>n</i> -Butyl	.0500	.0499
<i>n</i> -Butyl	.1000	.1003
<i>n</i> -Butyl	.2000	.2006
<i>Sec.</i> -butyl	.0500	.0501
<i>n</i> -Heptyl	.0500	.0496
<i>Sec.</i> -nonyl	.0500	.0503

Limitations of the Mercuric Chloride Method in the Presence of Naphthas and Unsaturated Hydrocarbons.—The mercuric chloride

method was applied without difficulty to *n*-butyl mercaptan in a naphtha ("Skellysolve") which was free from unsaturated hydrocarbons. In the presence of the latter, however, the method failed. Hofmann and Sand⁷ were the first to discover that mercuric chloride liberates hydrochloric acid when shaken with an unsaturated hydrocarbon of the olefin series. Several cubic centimeters of alkali was required to neutralize the acid when a 1% mercuric chloride solution was shaken for three minutes with a 1% solution of amylene in benzene.

Summary

1. The iodimetric method for the estimation of mercaptans has been applied to benzene solutions.
2. Two acidimetric methods for the estimation of mercaptans are given: in one the hydriodic acid formed in the iodimetric oxidation is titrated; in the second method, the hydrochloric acid liberated by the action of mercuric chloride on the mercaptan is estimated.

⁷ Hofmann and Sand, *Ber.*, **33**, 1349 (1900).

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE DEPARTMENT OF RESEARCH IN PURE CHEMISTRY, MELLON INSTITUTE OF INDUSTRIAL RESEARCH]

THE PROPERTIES OF *d*-MANNURONIC ACID LACTONE

BY WILLIAM L. NELSON AND LEONARD H. CRETCHER

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Since the publication of our paper on the isolation and identification of *d*-mannuronic acid lactone from *Macrocystis pyrifera*,¹ the lactone has been obtained in this Laboratory by hydrolysis of alginic acid from *Fucus serratus* and *Laminaria saccharina*.² As a result of our further work, we have discovered the mutarotation of the lactone which escaped our observation because of the small amount of the substance available in our earlier experiments.

The lactone was isolated through the cinchonine salt as previously described.¹ The melting point and optical rotation of the cinchonine salt from *Fucus serratus* and *Laminaria saccharina* agreed with the values reported for the salt from *Macrocystis pyrifera*.³ Under different conditions of hydrolysis, however, Schmidt and Vocke,⁴ Miwa⁵ and Bird and Haas⁶ have obtained salts with different properties.

¹ Nelson and Cretcher, *THIS JOURNAL*, **52**, 2130 (1930).

² We are indebted to Dr. E. J. Allen, Director of the Marine Biological Station, Plymouth, England, for his kindness in supplying us with these algae.

³ Cretcher and Nelson, *Science*, **67**, 537 (1928); Nelson and Cretcher, *THIS JOURNAL*, **51**, 1914 (1929).

⁴ Schmidt and Vocke, *Ber.*, **59**, 1585 (1926).

⁵ Miwa, *J. Chem. Soc. Japan*, **51**, 738 (1930).

⁶ Bird and Haas, *Biochem. J.*, **25**, 403 (1931).