

dilute acids or alkalis and inorganic solvents in general. Molecular weight determinations by the freezing point lowering method, when dissolved in benzene, gave values of 269, 270 and 272, which show that it is somewhat associated in benzene solution since the simple formula for $(\text{CH}_3\text{CS})_2\text{S}$ has a molecular weight of but 150.

Conclusions

1. The solubilities of the different types of organic compounds in liquid hydrogen sulfide have been observed.
2. The presence of a double bond in the organic compound is usually shown by the development of the odor of a mercaptan.
3. The aldehydes, amines and acyl halides are the only types that show much evidence of reacting with the liquid hydrogen sulfide.
4. The amines give unstable addition products with hydrogen sulfide.
5. The aldehydes tend to substitute a sulfur atom for the sulfur of the aldehyde group to form a thio-aldehyde.
6. The acyl halides tend to substitute an SH group for the halide and an S for the oxygen and form dithio acids to a small amount. Acetyl chloride and bromide form the dithioacetic acid, which then loses hydrogen sulfide and forms the thioanhydride.

AMES, IOWA

NOTES

A Sensitive Test for Magnesium.^{1,2}—K. Suitsu and K. Okuma³ state that the azo dye, *o,p*-dihydroxy-azo-*p*-nitrobenzene gives a very sensitive test for the magnesium ion. This reagent has been used in the courses of qualitative analysis at this University for two years with excellent results. The authors claim to be able to detect $1/500$ mg. of magnesium by means of this test.

The dye is readily prepared by diazotizing *p*-nitraniline and coupling it with the theoretical quantity of resorcinol dissolved in dilute sodium hydroxide solution. The solution is acidified and the precipitated dye filtered off. The product may be purified by recrystallization from methyl alcohol as a dark red powder, m. p., 199–200°. A convenient concentration for ordinary use is a 0.5% solution of the dye in 1% sodium hydroxide. Some deterioration of the reagent occurs in solution after a year's standing.

The solution to be tested for magnesium is made slightly acid with dilute hydrochloric acid and one drop of the reagent added. On making

¹ Hahn, *Ber.*, **57**, 1394 (1924); **60**, 975 (1927), describes a somewhat similar test for magnesium using 1,2,5,8-tetrahydroxy-anthraquinone.

² Since this note has been accepted for publication, the Eastman Kodak Company has informed me that they intend placing the reagent on the market.

³ Suitsu and Okuma, *J. Soc. Chem. Ind. Japan*, **29**, 132–138 (1926); *C. A.*, **20**, 3000 (1926).

the solution alkaline with dilute sodium hydroxide, the characteristic sky-blue precipitate of the magnesium lake appears. If the amount of magnesium is very small, a drop of the stock reagent which has been diluted 4 to 5 times with water gives better results. In this case also the lake is rather slow in forming and shaking for two to three minutes is necessary to coagulate the precipitate.

Professor D. P. Smith of this University found that an excess of ammonium salts destroys the sensitivity of the reagent; hence in the regular course of analysis, the ammonium salts are "smoked off" in a casserole before applying the test.

Nickel and cobalt also give somewhat similar blue lakes which may lead to confusion. After the removal of the heavy metals by precipitation as sulfides, however, the test is absolutely characteristic and the confusion attending the use of the classical magnesium ammonium phosphate precipitate as a test, especially in elementary courses of analysis, is obviated.

CONTRIBUTION FROM THE
DEPARTMENT OF CHEMISTRY
PRINCETON UNIVERSITY
PRINCETON, NEW JERSEY
RECEIVED NOVEMBER 14, 1928
PUBLISHED MAY 6, 1929

WM. L. RUIGH

The Preparation of Selenic Acid and its Salts.—A number of methods for the preparation of selenic acid have been reported in the literature.¹ As a rule the salts of this acid have been prepared by the oxidation of the selenites.

Meyer and Heider^{1a} treated selenium dioxide with 30% hydrogen peroxide, warming the mixture on the water-bath and upon analysis found that 48% of the oxide had been oxidized to selenic acid. In another experiment using a larger amount of hydrogen peroxide an analysis showed an oxidation of 70%.

The experiments of Meyer and Heider suggested that it might be worth while to try to find the best conditions for preparing selenic acid, and possibly the selenates, by the hydrogen peroxide method.

A number of experiments were carried out, treating weighed amounts of selenium dioxide with varying amounts of hydrogen peroxide. The time and the temperature of the treatment were varied. Oxidation values all the way from 20 to 70% were obtained. Small amounts of the oxide

¹ The methods for the preparation of selenic acid and its salts are found in the following references: (a) Meyer and Heider, *Ber.*, **48**, 1154 (1915); (b) Mitscherlich, *Pogg. Ann.*, **9**, 623 (1827); (c) Wohlwill, *Ann.*, **114**, 169 (1860); (d) *Wien Akad. Ber.*, **39**, 299 (1860); (e) Thomsen, *Ber.*, **2**, 598 (1869); (f) Diemer and Lenher, *J. Phys. Chem.*, **13**, 505 (1909); (g) Müller, *Ber.*, **36**, 4262 (1903); (h) *Chem.-Ztg.*, **31**, 630 (1907); (i) Meyer and Moldenhauer, *Z. anorg. Chem.*, **116**, 193 (1921); (j) Worsley and Baker, *J. Chem. Soc.*, **123**, 2870 (1923).

were then refluxed with 30% hydrogen peroxide, with the result that the oxidation values were much higher. These results were reproducible as is shown in the following table.

TABLE I
RESULTS OF EXPERIMENTS

Selenium dioxide, g.	0.2019	0.2000	0.2029
Hydrogen peroxide, 30%, cc.	10	10	10
Time of refluxing, hours	2	2	2
Oxidation, %	89.5	90.7	91.9 *

A quantity of selenic acid was prepared, adhering to the conditions shown in Table I. The small amount of selenious acid was reduced to selenium, filtered off and the filtrate concentrated, following the procedure of Cameron and Macallan.² In this manner selenic acid of high purity with a concentration of 84% was readily prepared.

Since hydrogen peroxide proved so effective in oxidizing selenious acid, it seemed desirable to try its use for the oxidation of selenites to selenates. Copper selenite was prepared by treating copper carbonate with selenious acid. The green, insoluble copper selenite remained. This salt was covered with 30% hydrogen peroxide and refluxed for three hours, during which time it was oxidized to the blue, soluble selenate. A small amount of the insoluble selenite was filtered off, leaving a clear blue filtrate from which copper selenate crystals formed, identical in appearance to those of copper sulfate. Using the same procedure selenates of nickel, cobalt, aluminum and magnesium were prepared. All of these salts were obtained in a well defined, crystalline condition, similar to the corresponding sulfates.

CONTRIBUTION FROM THE
DEPARTMENT OF CHEMISTRY
SYRACUSE UNIVERSITY
SYRACUSE, NEW YORK
RECEIVED NOVEMBER 23, 1928
PUBLISHED MAY 6, 1929

ERNEST R. HUFF
C. R. McCrosky

Use of Cresol Red in Acid Solutions.—As has been pointed out by Clark¹ and Cohen,² the sulfonephthalein indicator dyes undergo two distinct color changes at different points on the P_H scale. However, of this series only thymol blue and meta cresol purple have been applied as indicators in both acid and alkaline solutions and the fact that the sulfonic acid dissociation of cresol red is sufficiently repressed so that it can be used in acid solutions has not been emphasized. This indicator is really

² Cameron and Macallan, *Chem. News*, **59**, 219 (1899).

¹ Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, Md., 1922, p. 93.

² Cohen, "U. S. Public Health Reports," **41**, 3051-3074 (1926).

quite valuable in certain cases. The color change is from red at P_H 0.2 to yellow at P_H 1.8, the half transformation point occurring at a hydrogen concentration of approximately 1.0×10^{-1} , or P_H 1.0. The virage resembles those of thymol blue and meta cresol purple over their acid ranges.

Cresol red can be used to advantage in testing for free mineral acids in solutions of weak acids, such as citric or acetic, or hydrolyzable salts of an acidic nature, such as ferric chloride or sulfate. It can also be employed in adjusting solutions in qualitative analysis, so as to separate the sulfides of the second and third groups. Cresol red is superior to methyl violet in that it is quite stable in solution and also gives stable, reproducible colors.

CONTRIBUTION FROM THE
RESEARCH LABORATORY
LAMOTTE CHEMICAL PRODUCTS CO.
BALTIMORE, MARYLAND
RECEIVED JANUARY 7, 1929
PUBLISHED MAY 6, 1929

F. R. McCRUMB
W. R. KENNY

The Rapid Concentration of Germanium and Gallium Contained in Zinc Oxide Carrying Them.—The method usually given for the extraction of germanium and gallium from zinc oxide carrying a small percentage of these elements, calls for solution in hydrochloric acid and the subjection of the whole solution to distillation, after oxidizing the arsenic with potassium chlorate or other suitable oxidizing agent. It has been found in the Laboratories of the University of New Hampshire that the two elements can be rapidly concentrated as follows.

The zinc oxide was dissolved in an excess of commercial hydrochloric acid, allowed to stand for a short time and the precipitate of lead chloride removed by filtration. The hot solution, while being thoroughly stirred, was then rendered basic by the slow addition of some of the original zinc oxide. After continuing the stirring for some time to make certain of the precipitation of all the germanium and gallium, the precipitate carrying them was filtered off, dissolved in hydrochloric acid, distilled and treated in the usual manner to obtain the two elements.

In order to ascertain the completeness of their precipitation by the treatment with zinc oxide, large portions of the filtrates from several different runs were strongly acidified with hydrochloric acid, the arsenic was oxidized with potassium chlorate, a portion distilled off and hydrogen sulfide passed into the distillate. The absence of any germanium sulfide was considered evidence that all but negligible quantities at least of that element had been removed. The liquid remaining in the flask after distillation was examined by means of the spark spectrum for gallium after any traces of it had been concentrated by neutralizing with ammonium hydroxide and rendering basic with metallic zinc, etc. The violet lines characteristic of it were not visible.

By employing this preliminary concentration 100 lb. of zinc oxide could be put through the distillation process in four or five runs using a 12-liter Pyrex flask, whereas before this method was used it required 25 to 30 runs; also, the quantity of material from that process which had to be worked over for gallium was correspondingly decreased.

CONTRIBUTION FROM THE
CHEMICAL LABORATORY OF THE
UNIVERSITY OF NEW HAMPSHIRE
DURHAM, NEW HAMPSHIRE
RECEIVED JANUARY 9, 1929
PUBLISHED MAY 6, 1929

C. JAMES
H. C. FOGG

Determination of Ethylene by Absorption in a Solution of Silver Nitrate.—During the course of a study of the catalytic hydrogenation of acetylene¹ the author observed that a solution of silver nitrate is capable of absorbing ethylene. A preliminary test at that time tended to indicate that the reaction might be used for the quantitative determination of the latter gas.

A search of the literature revealed that reactions between ethylene and silver salts have been previously observed by Ross and Trumbull,² Gluud and Schneider³ and Lommel and Engelhardt.⁴ The feasibility of using a solution of a silver salt alone as an absorbing medium in the determination of ethylene has apparently never been investigated.

Reactions between ethylene and salts of a few other metals have also been observed. In this connection, attention may be directed to the suggestion⁵ for the use of a solution of mercuric nitrate over mercury as a quantitative absorbing agent for this gas.

The apparatus used during a brief investigation of the usefulness of a solution of silver nitrate as an absorbent in the determination of ethylene has been described previously by the author.⁶ In its use the absorbing solution is passed slowly over and around the gaseous sample and is removed continuously at the bottom. Such an apparatus is particularly advantageous in cases where, as appeared to be probable in this case, there is a tendency toward an equilibrium condition involving incomplete absorption.

The table below records the results of a comparison of the absorption of ethylene from a mixture consisting essentially of nitrogen and ethylene by solutions of silver nitrate of various concentrations. The volumes of

¹ Morris and Reyerson, *J. Phys. Chem.*, **31**, 1332 (1927).

² Ross and Trumbull, *THIS JOURNAL*, **41**, 1180 (1919).

³ Gluud and Schneider, *Ber.*, **57B**, 254 (1924).

⁴ Lommel and Engelhardt, *ibid.*, **57B**, 848 (1924).

⁵ See Treadwell-Hall, "Quantitative Analysis," 7th ed., John Wiley and Sons, Inc., New York, p. 698.

⁶ Morris, *THIS JOURNAL*, **49**, 979 (1927).

solutions and the time requirements shown, while not necessarily representing the exact minima in every case, do give indication of what may be expected in a satisfactory operation carried out as rapidly as a careful observation of the progress of the absorption appears to justify.

TABLE I
THE ABSORPTION OF ETHYLENE BY SOLUTIONS OF SILVER NITRATE

Concn. of soln., %	40	20	10	5
Vol. of soln. used, cc.	12	28	40	80
Time for absorption, sec.	55	75	180	240
Red. in vol. of 50 cc. sample, cc.	34.8	34.9	34.9	34.7

The absorption by the more concentrated solutions was more rapid. The use of concentrated solutions is also recommended as a consequence of the fact that the completion of absorption can be more readily judged when using them rather than the slower absorbing dilute solutions.

In an additional experiment a comparison was made between a solution of silver nitrate and other reagents commonly used in the quantitative absorption of ethylene. The value for the ethylene content of a mixture of this gas with nitrogen as indicated by absorption with fuming sulfuric acid agreed closely with that obtained on the same mixture when a 20% solution of silver nitrate was used. The fact that absorption by bromine gave a slightly different value was attributed to a change in the composition of the gaseous mixture during the time interval between tests.

There are certain advantages in the use of silver nitrate for this purpose. It is interesting to note, for instance, that, in accordance with the observation of Lommel and Engelhardt,⁴ the ethylene may subsequently be removed from the solution by evacuation. Recovery of the absorbing solution is thus possible. Evaporation can readily be applied to restore it to the concentration desired for subsequent determinations. Whether heat alone would free the solution from ethylene as well as concentrate it remains to be investigated. A solution of silver nitrate has, moreover, a decided advantage over the commonly used absorbents, bromine and strong sulfuric acid, in that the chemical and physical properties of these latter make them anything but pleasant reagents to handle.

There are several points in connection with the reaction between ethylene and silver nitrate which seem to be worthy of further study. Of primary interest is the question of the composition and properties of the reaction product. The possibility of increasing the effectiveness of absorption by adding acids such as sulfuric or phosphoric to the solution of silver nitrate also merits investigation.⁴ As a final consideration attention may be directed to the fact that acetylene may be determined by titration of the nitric acid released when this gas reacts with a solution of silver nitrate. The possibility of determining both acetylene and ethylene in a mixture

of the two by the use of a single absorbing agent, a solution of silver nitrate, is at once apparent.

V. N. MORRIS⁷

RECEIVED JANUARY 12, 1929
PUBLISHED MAY 6, 1929

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, CHEMICAL DEPARTMENT OF THE CITY OF CHICAGO MUNICIPAL TUBERCULOSIS SANITARIUM]

MENTHOL STUDIES. II. MENTHYL ESTERS OF THE 2-NITRO-4-CARBOXYPHENYLARSONIC AND PHENYLARSENIOUS ACIDS

BY K. LUCILLE McCLUSKEY

RECEIVED OCTOBER 3, 1928

PUBLISHED MAY 6, 1929

The first report¹ on the synthesis of aromatic terpene compounds to be used in chemotherapeutic studies in experimental tuberculosis included menthyl esters of the nitro- and aminocinnamic acids. Due to the great insolubility in water caused by the menthol, the menthyl esters of the aminocinnamic acids could not be made water-soluble through their hydrochlorides. Since a water-soluble product is desirable, the introduction of arsenic into the aromatic terpene group was thought to be desirable for two reasons; first, to increase the solubility in water and second, to confer probably greater therapeutic properties.

A few organic arsenicals have been used in experimental studies in tuberculosis therapy, and arsenic in the form of arsenic acid was tried early in the treatment of tuberculosis. Sodium cacodylate, atoxyl, arsacetin and neosalvarsan have no tuberculocidal properties, according to Arkin and Corper,² but earlier investigators (Buchner, Weismayr, Pokhorow)³ comment favorably upon the worth of arsenic in the treatment of tuberculosis because of its favorable influence on metabolism, although they conclude that it is not a true chemotherapeutic agent with a specific action on human tubercle bacilli.

The new menthol arsenicals described here were made with the hope that they might possess some favorable pharmacological action.

Experimental

2-Nitro-4-methylphenylarsonic Acid.—This compound was first prepared by Jacobs, Heidelberger and Rolf⁴ using a different technique in the arsonation process from that described here. 3-Nitro-4-toluidine (110 g.) is stirred by means of a mechanical stirrer in 20% hydrochloric acid (500 cc.) until the hydrochloride is formed, and then diazotized at 0° with sodium nitrite (55 g.) dissolved in water (250 cc.). The diazo solu-

⁷ Present address—Firestone Tire and Rubber Company, Akron, Ohio.

¹ McCluskey and Sher, *THIS JOURNAL*, **49**, 452 (1927).

² Arkin and Corper, *J. Infectious Diseases*, **18**, 333 (1916).

³ Quoted by Weismayr in Ott's, "Chem. Path. der Tuberc.," **1903**, p. 480-481.

⁴ Jacobs, Heidelberger and Rolf, *THIS JOURNAL*, **40**, 1585 (1918).