1934

(The) preparation of meta-sulphobenzoic acid by the oxidation of meta-thiocresol.

BOSTON UNIVERSITY

GRADUATE SCHOOL

Thesis

THE PREPARATION OF META-SULPHO-BENZOIC ACID BY THE OXIDATION OF META-THIOCRESOL

by

Mary Clifford Rooney

(A.B., Emmanuel College, 1932)

submitted in partial fulfilment of the

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The author wishes to convey her gratitude to Doctor J. Philip Mason for his kind assistance, thoughtful consideration and indefatigable patience; also her appreciation to her laboratory colleagues for their helpful assistance.

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INTRODUCTION

The sulphonic acids offer an attractive field of endeavor for the organic chemist to explore. While these acids are, by no means newly discovered chemical compounds, they have not been treated and studied as fully as the other branches of organic chemistry. The importance of the sulphonic acids and their many derivatives have not been sufficiently impressed upon the student to warrant any greater than a passing interest in this subject.

Several commercial industries have made successful use of the properties of the sulphonic acids in the preparation of various products. Sulphonic compounds are indispensable in the manufacture of dyes[1] and have been employed in the synthesis of paints and varnishes.[2] One also finds that the properties of sulphonic acids and their derivatives are adaptable for medicinal purposes.[3]

It is the purpose of the investigator to synthesize meta-sulpho-benzoic acid by the oxidation of meta-thiocresol using as the oxidizing agent, potassium permanganate. The procedure used in this work is analogous to the one employed

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1 Allen's Commercial Org. Analysis , Vol.III p. 355

2 Chemistry for Engineers and Manufacturers Blount, B. and Bloxam, A. G., Vol. II, p. 366

3 Steiglitz, J., Chemistry in Medicine, p. 469

by Levene and Mikeska[4] in the preparation of several sulphonic acids and similar in some details to Reychler's[5] method of preparing cetyl sulphonic acid. It has been attempted to follow closely these procedures, but certain difficulties which arise have, at times, made this impossible. These deviations will be clearly shown later in this work.

It is the earnest desire of the author to isolate meta-sulpho-benzoic acid as the free acid. Every means will be used to achieve this end. However, to date, the sulphonic acids have been isolated generally as metallic sulphonates.

Since the literature concerning the preparation of meta-sulpho-benzoic acid is extremely scarce, it has been necessary to consider those methods for the preparation of sulphonic acids in general which may be adapted to the preparation of meta-sulpho-benzoic acid.

In this work, the author has tried to present a brief survey of sulphonic acids and the factors contributing to their formation, so that after reading this thesis, it is hoped that one has in brief, a clear knowledge of the most important chemical and physical properties of the compounds concerned in the preparation of meta-sulpho-benzoic acid and adequate information on the acid itself.

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[4] J. Biol. Chem., 65, 515-18 (1925)
[5] Bull. Soc. Chem. Belge, 27, 110-130 (1913)

METHODS OF PREPARATION OF THE SULPHONIC ACIDS AND META-SULPHO-BENZOIC ACID

A.

(1) When sulfuric acid is heated to 170° and benzene vapour is passed into it, the acid is converted into benzene sulphonic acid.[1] The concentration of the sulphuric acid should not fall below 64 percent, or the sulphonation will stop.

(2) Sulphonic acids have also been prepared[2] from unsaturated hydroaromatic hydrocarbons or their derivatives. These compounds (hydroaromatic hydrocarbons or derivatives) were treated with sulphonating agents in the presence of such substances which will form, with the sulphonating agents, onium compounds.

(3) Dachlauer and Thiel[3] prepared aromatic sulphonic acids by treating a mixture of aromatic hydrocarbons and methyl or ethyl alcohol with $ClSO_2OH$ or with fuming sulphuric acid at a high temperature (110-130°).

(4) By the oxidation of sulphinic acids[4] the corresponding sulphonic acids were prepared. The sulphinic acids obtained from their amides by Gatterman's diazo-reaction were oxidized by potassium permanganate in alkaline solution or

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1 A.G. Holleman, A Text Book of Organic Chemistry, p.313
2 C.A. - 23, 3716. Fr. 654,080, May 11, 1928
3 Ibid.
4 E. deB. Barnett, The Prep. of Org. Cmpds., p. 231

by treating the ferric salt of the sulphinic acids with NH_4OH and sodium hypochlorite; the resulting sulphonamide is decomposed by boiling with dilute alkali. When the sulphonic acid cannot be obtained by direct sulphonation, this method can be used.

(5) Bamberger[5] has demonstrated experimentally that sulphonic acid may be prepared from the sulphates of aniline. He successfully prepared phenyl sulphamic acid ($C_6H_5NHSO_2OH$) from the aniline sulphate by the elimination of water.

(6) Dodgson[6] has prepared sulphonic acids from the reduction of p-benzoquinone and its substituted derivatives by SO_2 alone or in alkaline medium. In the latter the production of the sulfonate is greatly increased. However, prolonged addition of the alkali almost completely prevents the reaction.

(7) Sulpho-benzoic acids[7] may be obtained by passing ozone, ozonized oxygen or ozonized air into a heated mixture of toluene and sulphuric acid or a heated solution of toluene sulphonic acid.

(8) Micheal[8] records the preparation of ortho-sulphobenzoic acid from the benzoic sulphimide by (a) boiling with $Ba(OH)_2$; (b) heating in a closed tube with conc. HCl; (c) evaporating on a water bath with HCl. This last method is the

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5 Ber. 26, 496 (1893)
6 C.A. 25, 691 (1931); 9, 206 (1915); Jour. Chem. Soc. (1930) 2498-2502; 105, 2435-43 (1914)
7 C.A. 10, 1579; Brit. 23, 575, Dec. 4, 1914
8 Am. Chem. Jour. 9, p. 405 (1887)

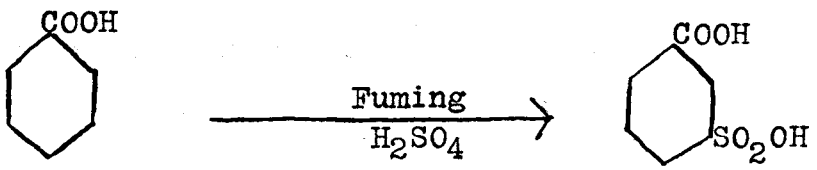
best and required 2 days, the acid being renewed from time to time. The liquid was finally evaporated to dryness and the residue dissolved in a small amount of waterand evaporated slowly.

(9) The oxidation of mercaptans[9] yields sulphonic acids. The oxidizing agents used may be concentrated sulphuric acid, nitric acid, potassium permanganate and the like. There are many theories as to the intermediate products of the oxidation, but it is agreed that the first step in the oxidation is the disulphide formation, and the last step the sulphonic acid.

$$RSH \xrightarrow{3\ (O)} RSO_2OH$$

B:

(1) One of the most successful and most frequently used methods of preparing meta-sulpho-benzoic acid is the direct[10] sulphonation of benzoic acid with fuming sulphuric acid



The meta acid is obtained along with the para derivative, but in the presence of mercuric sulphate[11] the ortho is

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9 Chem. Reviews 7, 515 (1930)

10 Lassar-Cohn, Arbeits Methoden fur Org. Chem. Lab. II, 108

11 P. Sabtier, Catalysis in Org. Chem., p. 316

obtained. While it is known that meta-sulpho-benzoic acid is the chief product of the sulphonation of benzoic acid, it is not know to what extent the ortho and para isomers are formed under various conditions. J. Maarse[12] has written a most instructive treatise on this subject. This article may be summarized as follows:

In these experiments on sulphonation, Maarse used 100 percent H_2SO_4, kept the temperature at 140°C. and filled the jacket of the condenser with xylene. The percentage of the meta acid formed during the experiments vary with the time consumed in the heating of the sulphonation mixture.

1.1 - 1.5 hours -- 96.4 percent meta-sulpho-benzoic acid formed.
6 " -- 94.5 " " " " " "
9 " -- 95.5 " " " " " "
24 " -- 97-99 " " " " " "

(2) By the action of an alcoholic solution of sulphur dioxide on meta-diazo-benzoic acid, Wiesinger and Vollbrecht[13] were able to prepare meta-sulpho-benzoic acid.

(3) Kafka[14] oxidized meta-sulpho-benzoic aldehyde with air at 95° and obtained meta-sulpho-benzoic acid.

(4) Oppenheim[15] found that by treating benzoyl chloride

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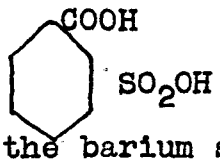
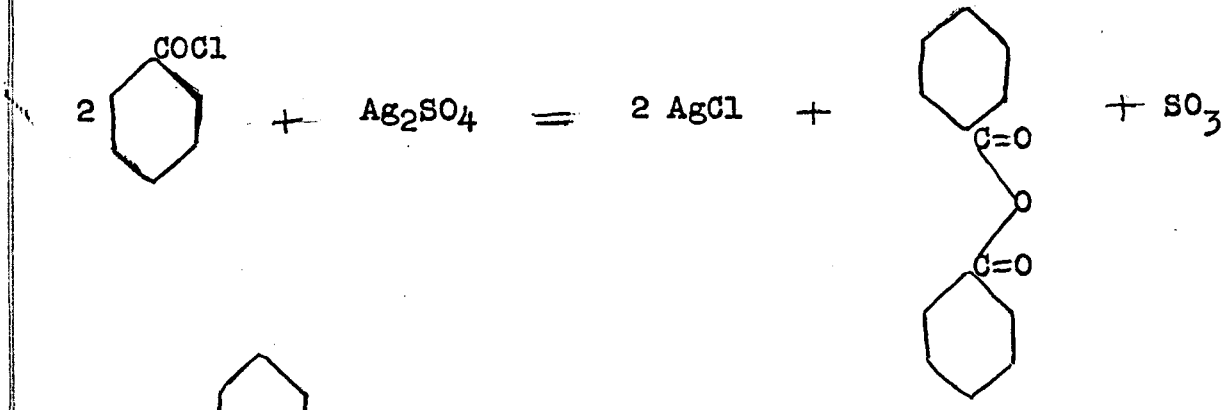
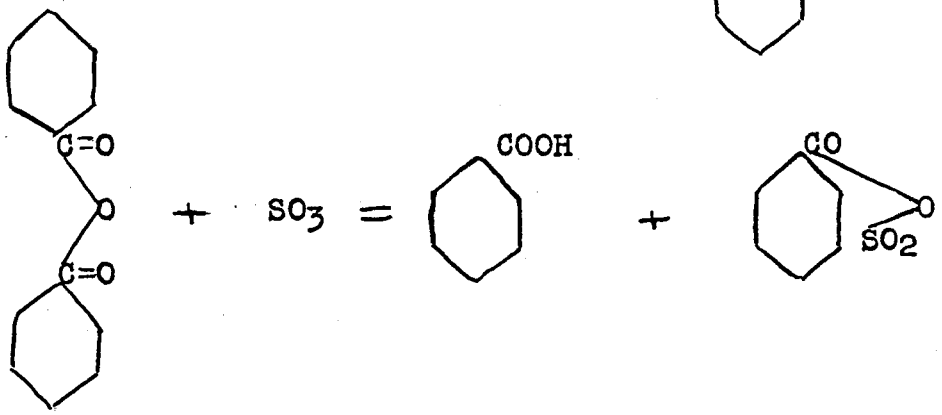
12 C.A. 9, 440 (1915),Rec. Trav. Chim., 33, 207.38 (1914)
13 Ber. 10, 1715
14 Ber. 24, 796
15 Ber. 3, 735; Jour. Chem. Soc., 24, 131

with sulphuric acid, meta-sulpho-benzoic acid was formed. The acid $C_6H_5COCl + H_2SO4 = HCl + C_6H_5COSO_4H$

isomer 

was extracted as the barium salt. Kammerer and Carius[16] also used benzoyl chloride in the preparation of the acid by heating it with silver sulphate at 150°C. They record the reaction in the following equations:





(5) In conducting the vapours of sulphur trioxide into benzoic acid, the chief product obtained is meta-sulpho-benzoic acid and in small amounts the para derivative. Mitscherlich[17] and Barth[18] prepared the sulphonic acid in this manner. R. Nakaseko[19] gives a detailed explanation of his experiment which is, in brief, as follows:- benzoic acid is fused and after

16 Ber. 4, 219
17 Pogg. Ann. 31, 287
18 A. 148, 33
19 Am. Chem. Jour. 47, 432-433

solidification, reduced to a fine powder and placed in a large balloon flask. SO_3 is introduced from a retort containing fuming H_2SO_4 (considerable heat evolved). When the mass is completely liquified, a few cc. more of H_2SO_4 are added. The mixture is heated over a low flame for several hours and allowed to stand over night. Unchanged benzoic acid is precipitated and filtered off. The filtrate is neutralized by $CaCO_3$and is subjected to decomposition by K_2CO_3. The potassium salt of meta-sulpho-benzoic acid is extracted by 95 percent alcohol and recrystallized from water.

PROPERTIES OF SULPHONIC ACIDS

I

It may be well, at this point, to discuss the most important of the characteristic properties of the sulphonic acids in general before dealing with those of meta-sulphobenzoic acid in particular.

Sulphonic acids[1] are strongly acidic, reddening blue litmus. They are extremely soluble in water, in some cases being hygroscopic, and frequently their well crystallized salts contain water of crystallization. Many of the sulphonic acids decompose on heating and hence have no definite melting point. The majority of the sulphonic acids are insoluble in cold sulphuric acid[2] and in ether. Sulphonic acids form soluble salts with metals.

On heating with HCl[3] under reduced pressure or with H_2SO_4 in a current of steam, the sulphonic groups split off from the sulphonic acids.

$$C_6H_5SO_3H \xrightarrow[H_2O]{H_2SO_4} C_6H_6 + 2H_2SO_4$$

Armstrong discovered this reaction, and Schmitt[4] and Ghetz

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[1] Cohen, J.B., Theor. Org. Chem., p. 430-431
[2] Gattermann, L., The Practical Methods of Organic Chemistry pp. 282-285
[3] Ibid., p. 283
[4] Lassar-Cohn, Organic Laboratory Methods, p. 240

showed that this group could also be removed by heating in an open vessel with HCl.

By the fusion[5] of a salt of a sulphonic acid with potassium or sodium hydroxide, a phenol is produced. This is a very

$$C_6H_5SO_3Na + NaOH \longrightarrow C_6H_5OH + Na_2SO_3$$

important method of manufacturing phenols. Alkali sulphonates also fuse with potassium cyanide.

$$C_6H_5SO_3K + KCN \longrightarrow C_6H_5CN + K_2SO_3$$

The prolonged reduction of sulphonic acids[6] yields thiophenols. This may be achieved by using zinc dust and sulphuric acid, the intermediate product being a sulphinic acid.

$$C_6H_5SO_2OH \longrightarrow C_6H_5SOOH \longrightarrow C_6H_5SH$$

By the action of phosphorous pentachloride on the salt[7] of the acid, or in some cases thionyl chloride on the free acid, the sulphonyl chlorides are produced.

$$C_6H_5SO_3Na + PCl_5 = C_6H_5SO_2Cl + POCl_3 + NaCl$$

$$C_6H_5SO_2OH + SOCl_2 = C_6H_5SO_2Cl + SO_2 + HCl$$

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5 W.A. Noyes, Organic Chemistry, p. 99

6 A. F. Holleman, A Textbook of Organic Chemistry, p. 373

7 H. T. Clarke, A Handbook of Organic Analysis, Qualitative and Quantitative, p. 97

Sulphonic acid chlorides[8] are crystalline solids with unusually low melting points, and possess the characteristics common to all acid chlorides. They combine with NH_3 and with primary and secondary amines.

$$C_6H_5SO_2Cl + 2\ NH_3 = C_6H_5SO_2NH_2 + NH_4Cl$$

$$C_6H_5SO_2Cl + 2\ NH_2C_6H_5 = C_6H_5SO_2NHC_6H_5 + C_6H_5NH_2HCl$$

Both the sulphonamides and sulphonanilides are sparingly soluble in water and are easily separated from other products of reaction. They are frequently used as derivatives for the identification of the sulphonic acids.

II It is reasonable to assume that meta-sulpho-benzoic acid will conform, in regard to properties, with the sulphonic acids in general. However, to date, no definite evidence has been found concerning the chemical properties of meta-sulpho-benzoic acid other than the fact that the acid has been isolated as various metallic salts; showing that it reacts with metals. The physical properties of the acid are quite definitely described.

In Watts[9] Dictionary of Chemistry the appearance of meta-sulpho-benzoic acid is recorded as a deliquescent crystalline mass.

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[8] J.B.Cohen, Theoretical Organic Chemistry, p. 430

[9] Watts, Dictionary of Chemistry, p. 594, Vol. IV

Solubility of the Sulpho-benzoic Acids[10]

	H_2O	alcohol	ether	acetone
ortho	sol.	v.s.	insol.	--
meta	deliq.	v.s.[11]	v.s.	v.s.[11]
para	v.s.	v.s.	v.s.	--

Melting Point and Form

ortho	130 C.	anhydrous	-- large trimet. crystals
meta	141 C.	"	almost colorless crystals[11]
para	260 C.	"	needles

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10 C.A. Hodgeman (ed.), Handbook of Chemistry and Physics
11 Beilstein, Band XI/XII p. 98

CONSTITUTION OF SULPHONIC ACIDS

Before introducing the experimental evidence favoring the possibility of forming meta-sulpho-benzoic acid by the oxidation of meta-thiocresol, it is advisable to show that such compounds are theoretically possible. Since oxidation is the essential process in this work, it is well to realize that "the constitution of compounds affects the rate of oxidation more than composition. Other conditions being the same, a saturated compound is less active than a non-saturated one."[1]

In dealing with the structural possibilities of these compounds, namely the mercaptan and the sulphonic acid, it may be well to consider for a moment the structure of benzene from which the aromatic compounds are assumed to be derived.[2] Kekulè started with this assumption, since all aromatic substances contain at least six carbon atoms, and although various modified formulae have been proposed for benzene, "the original idea[3] that six carbon atoms are members of one close ring still holds." Baeyer and Stohmann[4] show very definitely that this ring formation is extremely stable and differs radically in this respect from the unsaturated aliphatic compounds. However, it must not be assumed that every benzene type of ring compound is

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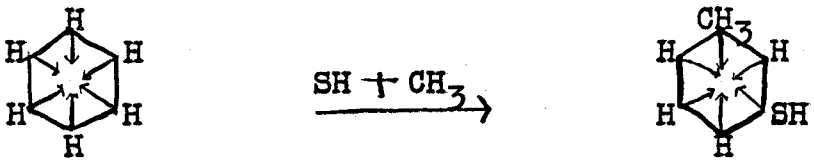
[1] J. Chem. Soc. A - 24 (1888), p. 25
[2] F. Henrich, Theories of Organic Chemistry, p. 161
[3] G. Pope, Modern Research in Organic Chemistry, p. IX
[4] Henrich, loc. cit.

saturated.

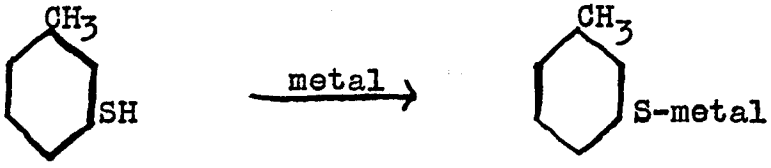
The formula suggested by Armstrong[5] clearly shows the fourth valence of the carbon atom and the possibilities for the substitution in the benzene ring.

The Armstrong formula is

With these facts in mind, it is theoretically possible to visualize the mercaptan (meta-thiocresol) and its corresponding sulphonic acid (meta-sulpho-benzoic acid). Thus by substituting the mercapto and methyl groups in the 1-3 position in Armstrong's formula, the meta-thiocresol is formed.



The sulphur[6] in the mercaptan is linked to the carbon of the radical or nucleus. In the mercaptan, there is only one molecule replaceable by metals. It can be reasonably assumed that this hydrogen distinguishable, from all others, is in union with the sulphur, while the other hydrogen atoms are attached to the carbon of the ring.



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5 Jour, Chem. Soc., 51, 264 (1887)
6 J.B.Cohen, Theoretical Organic Chemistry, p. 186

Oxidizing agents[7] convert the mercapto group into the sulphonic group without difficulty.

$$RSH \xrightarrow{(O)} RSO_2OH$$

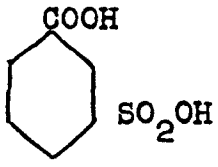
Since the sulphur in the mercaptans is in direct union with the carbon of the nucleus, the sulphonic acids have an analogous constitution, the sulphur[8] being directly attached to the carbon atom of the nucleus and not by means of an oxygen atom. The reduction[8] of sulphonyl chloride to a mercaptan demonstrates this fact.

$$C_6H_5SO_2Cl + 6\,H = C_6H_5SH + 2\,H_2O + HCl$$

The acidic character of the sulphonic acid points to the presence of the hydroxyl group. This is confirmed by the action of phosphorous pentachloride on the sulphonic acid, producing sulphonyl chloride.

$$C_6H_5SO_3H + PCl_5 \longrightarrow C_6H_5SO_2Cl + POCl_3 + HCl$$

The formula of the meta-sulpho-benzoic acid may be thus represented.



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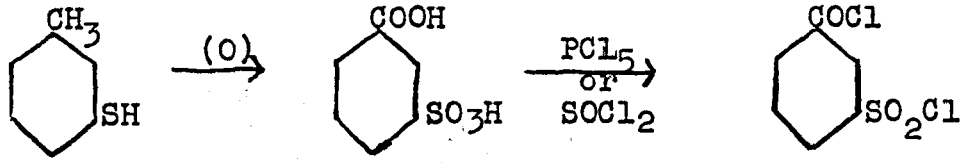
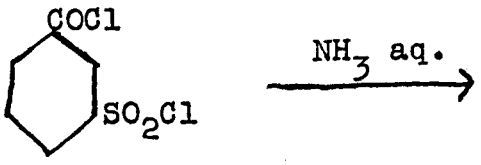
7 W.A.Noyes, Organic Chemistry, p. 98
8 J.B.Cohen, loc. cit.

It is now possible to show by formulae the compounds the investigator intends to obtain starting with the mercaptan.



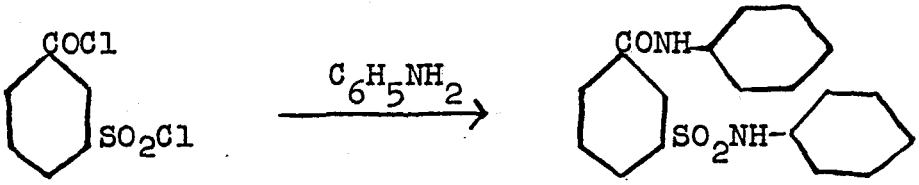
sulphonyl chloride

(A)



sulphonyl amide

(B)



sulphonyl anilide

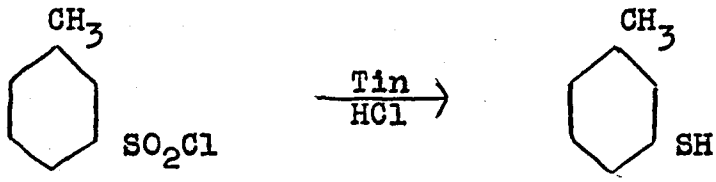
PREPARATION AND PROPERTIES OF MERCAPTANS

A. Preparation.

In presenting the preparation of meta-sulpho-benzoic acid from oxidized meta-thiocresol, it is necessary in treating the subject adequately, to discuss briefly mercaptans, their preparation and properties.

(1) Mercaptans can be prepared quite readily by treating mercaptides with mineral acids[1] and by the action of phosphorous pentasulphide on alcohols.[2]

(2) The sulphonyl chlorides of the aromatic acids were employed by Hübner and Post[3] in the preparation of mercaptans. They treated the sulphonyl chloride with tin and hydrochloric acid and as a result of the reduction, the mercaptan was formed.



(3) Alcoholic potassium hydrogen sulphide has been successfully used by Levene and Mikeska[4] in the formation of the mercaptans. These investigators prepared 2 mercapto-iso-

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1 A. F. Holleman, A Text Book of Organic Chemistry, p.71
2 Ibid.
3 J.Chem.Soc., 27 (1874), p. 81; 169, 51
4 J.Biol.Chem., 65, 515-18 (1925)

hexane as follows: 28 grams of L-2-iodoisohexane were treated with two equivalents of alcoholic potassium hydrogen sulphide and heated under reflux at 60-65°C. for five hours. The reaction mixture was poured into water in which an oil separated. This oil was extracted, washed with a little water and dried over sodium sulphite. The yield of the mercaptan was two grams.

(a) L-benzyl-phenyl-mercapto-methane was prepared by Levene and Mikeska[5] by treating 14 grams of 1 benzyl-phenyl-methane with 3 mols of alcoholic hydrogen sulphide solution. After standing 1½ hours, the mixture was heated for 2 hours on a steam bath. The mercaptan was isolated by pouring the mixture into water and extracting with ether which was removed by distillation under reduced pressure, at 50°C. (as mercaptan decomposes at a higher temperature). The investigators do not name the ether used. It was evidentally not ethyl ether which boils at 35°C. The mercaptan was washed with water and dried over sodium sulphate.

(4) Reychler[6] prepared cetyl mercaptan by treating 50 grams of cetyl iodide $C_{16}H_{33}I$, with an alcoholic solution of sodium hydrosulphide (4 grams Na; H_2S in excess, 160 grams abs. alc.). The reaction took place very satisfactorily and the mercaptan was isolated by the addition of water.

(5) By boiling meta-tolyl-ethyl xanthate with alcoholic potash, meta-thiocresol can be prepared.[7]

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5 J. Biol. Chem., 65, 515-18 (1925)
6 Bull. Soc. Chim. Belge 27, 110-130 (1913)
7 Watts Dictionary of Chemistry, p. 783

B. Properties.

Mercaptans or thioalcohols differ from ordinary alcohols as hydrogen sulphide differs from water[8]. They are acids and form well-defined salts with mercury (this characteric accounts for their name). Mercaptans possess an unpleasant garlic-like odor.[9] They are insoluble in water but dissolve in alkali solutions. They have boiling points which are markedly lower than those of alcohols.

Oxidizing agents easily convert the mercapto group (SH) to the sulphonic group (SO_2OH). This is one of the most important properties of the mercaptans. The agents most commonly used are nitric acid and potassium permanganate.

Meta-thiocresol (or tolyl-mercaptan) is a colorless oily liquid having an intense odor of mercaptan. It has a boiling point ranging from 194.5[10] to 200°C.[11] Meta-thiocresol is volatile in air, and, in ammoniacal alcoholic solution is oxidized by air to meta-tolyl disulphide. It is also oxidized by oxidizing agents to meta-sulpho-benzoic acid.

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8 W.A.Noyes, Organic Chemistry, p. 98
9 J.B.Colman and F. Arnall, The Preparation of Organic Compounds, p. 192
10 C.A.Hodgeman (Ed.), Handbook of Chemistry and Physics,
11 Watt's Dictionary of Chemistry, p. 783

POSSIBILITIES OF OXIDATION OF MERCAPTANS TO SULPHONIC ACIDS

It is the object of this thesis to definitely prove that from the evidence reliably obtained (as well as from experimental proof) concerning the oxidation of mercaptans to sulphonic acid that it is possible to obtain meta-sulpho-benzoic acid from the oxidation of the corresponding mercaptan, namely meta-thiocresol.

Therefore it was necessary to give careful consideration to the oxidizing agents available. In deciding upon the agent to be used the investigator was concerned in particular with two details.

(1) A fairly rapid oxidation which would give the best results; and

(2) At the same time an oxidation which could be accomplished with reasonable safety.

A definition of the term oxidation may be, at this time, most timely. Friend[1] defines oxidation as "the addition of oxygen to substances, the subtraction of hydrogen and the increasing of the electro-negative atoms or radicals in the molecule or the diminution of the electro-positive atoms". Henrich[2] also defines oxidation according to the electronic conception of chemical change.

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[1] J.N.Friend, A Text Book of Inorganic Chemistry, Vol. I, p. 15
R.M.Caven, The Foundation of Chemical Theory, p. 238

[2] F. Henrich, Theories of Organic Chemistry, p. 111

Delépine[3] suggests that organic compounds containing doubly linked sulphur atoms may be oxidized by air at ordinary temperatures (auto-oxidation). This oxidation is characterised by the evolution of fumes and the appearance of light. Whether or not mercaptans belong to the class of compounds capable of being so oxidized has not been stated.

The oxidizing agents given most careful consideration were nitric acid and potassium permanganate, while hydrogen peroxide and superoxol were tested only experimentally. Of the several oxidizing agents used in various experiments, $KMnO_4$ and HNO_3 were preferred; of theses two, $KMnO_4$ was the more suitable.

It was thought, at first, that these two reagents could be used together. The HNO_3 oxidizing the mercapto group, and the $KMnO_4$ the methyl group. This was found to be impractical experimentally.

A. Nitric Acid.

In the study of the oxidizing powers of HNO_3, it was found that this reagent was generally accepted as a good oxidizing agent. Lassar Cohn[4] says that nitric acid containing 76 percent oxygen makes an excellent oxidizing agent. It has been stated by Schorger[5] that it is possible to oxidize organic substances held in solution or suspension by HNO_3.

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[3] C.A. 16 - 248 (Compt. Rend.) 74 - 1291-3 (1922)

[4] Arbeits Methodien Für Organische Chemische Laboratorien Lassar Cohn, p. 744

[5] C.A. - 16 (1922), p. 1100 ; Can. 213, 177, Aug. 30, 1921

However, he does not designate the compounds so oxidized. The method employed may be outlined as follows: after treatment with HNO_3, the oxides of nitrogen are drawn off from the solution and oxidized by air or oxygen. These oxides are then absorbed by the mother liquid which is further oxidized.

Malisoff,[6] Marks and Hess mention, in passing, the possibility of oxidizing mercaptans by HNO_3. However, these same chemists state that, in spite of the frequency of such oxidations, they have not been studied in detail. Perhaps, this accounts for the lack of sufficient literature concerning the essentials of mercaptan oxidations by HNO_3. Nitric acid has been responsible for the entire removal[7] of the mercapto group in oxidizing arylimidazâle mercaptans. Grabowsky[8] offers further evidence as to the possibility of oxidation of mercaptans by HNO_3. He oxidized the mercapto group of normal butyl mercaptan to the sulphonic group. Meyer[9] succeeded in oxidizing a methyl group in combination with the benzene ring (chloronitrotoluene to chloronitrobenzoic acid) using dilute HNO_3 (sp. gr. 1.37). This oxidation took 62 hours; but this length of time is attributed to the presence of the halogen.

Leveneand Mikeska[10] were successful in oxidizing a

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[6] Chem. Reviews. VII, p. 515 (1930); Ber. 52, 1401 (1910)
[7] Chem. Reviews VII, 5150 (1930). A. 284, 9 (1895)
[8] J. Chem. Soc. 1875, p. 881 and 1175
[9] Lassar Cohn, Arbeits Methoden Für Organische Chemische Laboratorien, p. 745
[10] J. Biol. Chem. 65 - 515-18 (1925)

mercaptan by HNO_3. They carried out several mercaptan oxidations and it is interesting to note that in only one instance did they use HNO_3; $KMnO_4$ was employed in the other oxidations. The procedure followed in the HNO_3 oxidation is briefly outlined: 5 grams of mercapto iso-hexane were oxidized by heating under reflux for 1½ hours with 8 cc. of conc. HNO_3 and 2 cc. of H_2O. The mixture was placed in an evaporating dish, over a water bath, and concentrated nearly to dryness. A little water was added and the mixture evaporated again (this procedure was repeated until all HNO_3 was removed). The barium salt was then isolated.

Malisoff,[11] Marks and Hess say, nevertheless, that more definite results may be expected with permanganate. Thus the evidence presented has substantiated the belief that HNO_3 is a good oxidizing agent. However, it has not been used to any extensive degree in the oxidation of mercaptans to sulphonic acids. Reychler[12] in his article L'Acide Cetylsulfonique advises the use of $KMnO_4$ in preference to HNO_3 (fuming acid in this case). This chemist testifies to the violent and explosive reactive power of HNO_3; and in comparing the oxidation of HNO_3 with that of $KMnO_4$ says "the oxidation with potassium permanganate is easily moderated".

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[11] loc. cit.

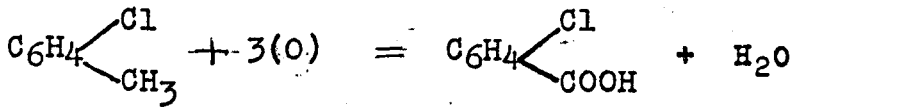
[12] Bull. Soc. Chim. Belge, 27, 110-130 (1913)

B. Potassium Permanganate.

Permanganates are powerful oxidizing agents.[13] Large quantities have been used in industry for the oxidation of organic compounds. Their use in the experimental laboratory is described in the following pages.

Potassium permanganate has been used successfully in the oxidation of mercaptans to sulphonic acids by Levene and Mikeska[14] and Reychler.[15] Levene and Mikeska used acetone as the solvent for $KMnO_4$, while Reychler used water. In both methods it is advisable to keep the temperature of the solution below 100° C. Reychler says that the temperature should be slightly below 100° C.; Levene and Mikeska report that in their experiments the solutions were at room temperature.

There is much evidence favoring permanganate oxidation. As it is the object of this work to obtain a complete oxidation of meta-thiocresol, the oxidation of the methyl and mercapto groups is of great importance. It is interesting to note that Ullman[16] oxidized the methyl group of chlorotoluene by means of an aqueous solution of permanganate. Here, as in the case of meta-thiocresol, the methyl group is directly joined to the ring. The time consumed in the oxidation of this group



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13 W.P.Ostwald, The Principles of Inorganic Chemistry, p. 604

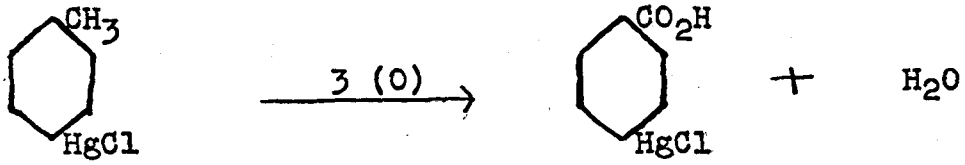
14 J. Biol. Chem. 65 - 515-518 (1925)

15 loc. cit.

16 Am. Chem. Jour. 16, 533; Lassar Cohn, Arbeits Methoden Für Organische Chemische Laboratorien, p. 699

was 12-15 hours; 60 grams of chlorotoluene were used and the concentration of the permanganate solution was 150 grams to 3 liters of H_2O.

Whitmore and Woodward[17] also show that the methyl group is readily oxidized by $KMnO_4$. In this case, an alkaline solution of the permanganate was used. P-tolylmercuric chloride was oxidized to para-chloromercuri-benzoic acid.



To oxidize 500 gm. of the chloride required 720 gm. of $KMnO_4$ in a solution of NaOH (1200 gm. of NaOH in 18 liters of H_2O). The mixture was mechanically stirred and the highest possible temperature was 95°C.

Further evidence as to the possibility of oxidizing the methyl group with $KMnO_4$ is offered by Weith.[18] Again the experiment was carried out in an alkaline medium, an excess of caustic soda solution being the solvent for pure ortho toluic acid. The solution was mixed, and to it was immediately added the calculated amount of $KMnO_4$. The mixture was heated for 10 hours on a water bath. The reaction may be indicated by the following equation:-

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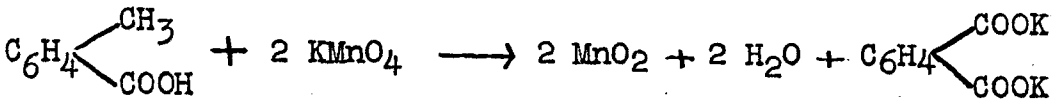
17 Organic Synthesis, Collective Volume I, p. 153
18 Lassar Cohn, Arbeits Methoden für Organische Chemische Laboratorien, p. 704; Ber. 7, 1058



It is generally agreed that in the oxidation of mercaptans to corresponding sulphonic acids, the conversion of the SH group to SO_2OH is readily accomplished. Most text books[19] are in accord in offering as an accepted fact the authenticity of this reaction, employing different oxidizing agents. In addition to this, much experimental evidence has been offered verifying the oxidation of the SH group. It is some times possible to oxidize[20] the mercapto group by air alone. To refer again to Malisoff,[21] Marks and Hess, their article states "it is difficult to keep a solution of mercaptans in oil from oxidizing".

Coleman and Arnall[22] do not point out any difficulties in the oxidation of thiophenols to sulphonic acids and say in passing that mercaptans are "easily oxidized by HNO_3 or $KMnO_4$ to sulphonic acids".

Autenrieth[23] has oxidized ethyl mercaptan to the sulphonic acid by potassium permanganate. The mercapto group was readily oxidized.

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19 A.F.Holleman, A Text Book of Organic Chemistry, pp. 74, 357, 373
J.B.Cohen, Theoretical Organic Chemistry, p. 186
W.A.Noyes, Organic Chemistry

20 A. 149, 247 (1869)

21 Chemical Reviews VII p.515 (1930)

22 Coleman and Arnall, The Preparation and Analysis of Organic Compounds, p. 192

23 J. Chem. Soc. 1891 - 203

$$2\ KMnO_4 + H_2O \longrightarrow 3(O) + 2\ MnO_2 + 2\ KOH$$

$$C_2H_5SH \xrightarrow{3\ (O)} C_2H_5SO_2OH$$

As has been mentioned Delépine[24] has testified to the ease of oxidation of compounds and Szeut-Gyorgyi concludes, after several experiments, "the SH groups bind molecular O_2 as a highly active peroxide".

Thus, it has been shown that potassium permanganate is an excellent oxidizing agent for the oxidation of mercaptans having considered the evidence showing the oxidation of the methyl and mercapto groups by this agent.

It may be well, at this point, to discuss the various solvents for $KMnO_4$, if a solution of the oxidizing agent is to be used.

As it is the intention of the investigator to use as far as possible, the procedure as outlined by Levene and Mikeska[25], it may be well to state a most essential precaution to be observed when using acetone as a solvent for $KMnO_4$ and the mercaptan. The acetone must be absolutely free from all oxidizable matter. Sachs[26] found it advisable when using acetone in this capacity to prepare the solvent as follows: the acetone was distilled several times above $KMnO_4$ until all the oxidizable material was removed from the acetone. This

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24 C.A. 16, 2481; 19, 307
25 J. Biol. Chem. 65 - 515-518 (1925)
26 Lassar Cohn, Arbeits Methoden Für Organisch-Chemische Laboratorien, p. 711
24 Compt. rend. 174, 291-3 (1924); Biochem. Z. 146, 245-53 (1924)

point can be easily recognized. When after refluxing for a considerable time (dependent upon the amount of oxidizable impurities present), the $KMnO_4$ is no longer reduced as shown by the failure of the MnO_2 to precipitate, the acetone is considered purified.

Water has been generally accepted as the most common solvent for $KMnO_4$. However, it is possible to use $KMnO_4$ in the solid state;[27] to liberate the oxygen, a temperature of 240° C. is needed. Since it is not feasible to raise the temperature this high, the use of solid $KMnO_4$ is not suitable. Water is an excellent solvent for the $KMnO_4$ despite the fact that $KMnO_4$ is slightly soluble in cold water. The following table[28] shows that the solubility increases with the temperature of the solvent.

100 grams of H_2O dissolves

Temperature	-0.58°	4°	10°	20°	40°	60°	75°
$KMnO_4$ in grams	3.0	3.4	4.4	6.5	12.5	22.0	32.4

Reychler[29] in contrast to Levene and Mikeska[30] used H_2O as the solvent for $KMnO_4$ in the oxidation of a mercaptan. He does not record just what was the weight of $KMnO_4$ in 800 grams of H_2O. Reychler[31] was successful in using a neutral solution

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27 G.S.Newth, A Text Book of Inorganic Chemistry, p. 670
28 Fritz Ephraim, A Text Book of Inorganic Chemistry, p. 384
29 Bull. Soc. Chim. Belge, 27 - 110-130 (1913)
30 J. Biol. Chem. 65 - 505-518 (1925)
31 loc. cit.

of $KMnO_4$. While not denying this, Brackett and Hayes[32] have found that in a neutral solution of $KMnO_4$ the oxidation of sodium toluene sulphonate to ortho sulpho-benzoic acid was extremely slow and not complete after 24 hours of boiling. By making the solution alkaline, they were able to lessen the time consumed to a few hours. The author has found, in the case of meta-thiocresol, an alkaline solution is just as ineffective (e.g. slow in reacting) as the neutral solution.

Gattermann[33] testifies to the fact that $KMnO_4$ oxidation may be accomplished in acidic as well as alkaline medium. (Of the two, in mercaptan oxidation, this author has found the acidic solution of $KMnO_4$ to be the more efficient.) The following equations explain the chemical reactions involved in $KMnO_4$ oxidation in the various mediums.

A. Alkaline:-

$$2\ KMnO_4 + H_2O \longrightarrow 3\ (O) + 2\ MnO_2 + 2\ KOH$$

B. Acidic:-

$$2\ KMnO_4 + 3\ H_2SO_4 \longrightarrow K_2SO_4 + 2\ MnSO_4 + 3\ H_2O + 5(O)$$

Gattermann suggests the use of 62-5 percent solution of $KMnO_4$, the excess of permanganate may be removed by sulphurous

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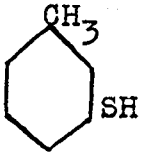
32 Am. Chem. Jour. 9, 403 (1887)
33 L. Gattermann, The Practical Methods of Organic Chemistry, p. 339

acid or alcohol - the former being oxidized to sulphuric acid, and the latter to aldehyde or acetic acid.

In considering the qualities of $KMnO_4$ oxidation, one must mention its defects which are not of too great importance in view of the efficiency of the $KMnO_4$ as an oxidizing agent. Manganous dioxide formed during the reduction of $KMnO_4$ exerts, to some degree, the influence of an anticatalyst,[34] tending to slow up the speed of the reaction. This has been noticed during the experimental work of this thesis. It is necessary, then, to remove the precipitate as frequently as possible but in doing so this precaution must be observed. Often times in $KMnO_4$ oxidation, there is a tendency for the reacting compound to cling to the MnO_2 precipitate.[35] It is advisable to boil this precipitate in a sufficient quantity of water and add this solution after filtering off the MnO_2 to the mother liquid.

While the time element is an important factor in oxidation, it must be remembered that the constitution of the compound to be oxidized influences greatly the rate of oxidation. A methyl group, such as in  (meta-thiocresol)

is one of the most firmly bound substituents[36] of the benzene ring and benzene derivatives are very slowly oxidized, needing the presence of heat or sunlight to accomplish the oxidation.

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[34] F. Henrich, Theories of Organic Chemistry, p. 181
[35] Organic Syntheses XIII, p. 5
[36] F. Henrich, Theories of Organic Chemistry, pp. 163, 181

ISOLATION OF THE SULPHONIC ACIDS

In the literature reviewed, the investigator has found very little data concerning the isolation of sulphonic acids, in the free state, and especially concerning the sulpho-benzoic acids. Brackett and Hayes[1] succeeded in obtaining the free ortho benzoic acid by the following procedure. The acid had been obtained as the potassium salt. The sulphates and free acid "are probably formed" by adding a slight excess of H_2SO_4. The solution is evaporated to dryness and treated with alcohol (75%) which extracts the greater part of the potassium salt of the acid -- (inorganic salts undissolved). The extract is evaporated and again extracted with alcohol. To this solution, $BaCO_3$ is added, and the solution filtered. Just enough H_2SO_4 is added to precipitate the barium. The solution contained the free acid which on evaporation crystallized out. The investigator notes, however, that the yield is extremely small. Another method[2], quite similar to the one used by Brackett and Hayes, is to precipitate the sulphate from the acidic aqueous solution by boiling barium (or calcium) carbonate. The solution is filtered and treated with H_2SO_4 drop by drop as long as a precipitate is produced. The solution is filtered again and the filtrate evaporated to dryness. The acid is recrystallized. If the calcium sulphonate

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1 Am. Chem. Jour. 9, 403 (1887)
2 Perkin and Kipping, Organic Chemistry, p.429

is present, add a little alcohol, filter and evaporate again.

The majority of the sulphonic acids prepared, have been extracted as the potassium, lead, sodium and barium salts of the acid.

Levene and Mikeska[3] extracted methyl phenyl methane sulphonic acid as potassium sulfonate. After evaporating the oxidation products to dryness, they saturated an alcoholic extraction with CO_2. The potassium sulphonate is precipitated.

Reychler[4] acidified the oxidation products with acetic acid, warmed the solution on a water bath and precipitated the salt of cetyl sulphonic acid as the lead salt. It is possible to decompose[5] the lead salt with sulphuretted hydrogen and remove the precipitated lead sulphide by filtering.

Richter[6] suggests that the sulpho-benzoic acids be separated from aqueous solutions in the form of their sodium salts by "salting out" with NaCl. The sodium salts[7] of the sulphonic acids are also extracted by rendering the solution (in this case the acid was produced by sulphonation) neutral or feebly alkaline and treating with dilute alcohol. The aqueous alcoholic layer is withdrawn and treated with NaCl. The sulphonate layer is extracted with ethyl alcohol.

The sulphonates[8] of the other metals may be obtained by

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3 J. Biol. Chem. 65 - 515-518 (1925)
4 Bull. Soc. Chim. Belge I 110-130 (1913)
5 L. Gattermann, The Practical Methods of Organic Chemistry, p. 283
6 V. Richter, Organic Chemistry - II p. 134; H.T.Clarke, A Handbook of Organic Analysis, p. 47
7 C.A. 26 - 1623 (1932), Ger. 539, 270, April 1, 1930
8 E. deB. Barnett, The Preparation of Organic Compounds, p. 231

neutralizing the acidic oxidation solution with the carbonate of the metal desired. The precipitated sulphate is removed by filtering while hot and is well washed with water. The filtrate is concentrated until crystallization takes place.

PROCEDURES

Since it is the object of the investigator to follow as far as it is possible the procedure of Levene and Mikeska[1] in the preparation of sulphonic acids, it may be well at this point to describe in detail their method. It is as follows:- "7 grams of levo-methyl-phenyl-mercapto methane were dissolved in 70 cc. of acetone and 10 cc. of water. Then 16.10 grams of potassium permanganate were added, in small amounts, with cooling, until the permanganate was no longer decolorized. The mixture was heated and during this heating an occasional addition of $KMnO_4$ was made until all the oxidizing agent had been consumed. The MnO_2 was then filtered off and the filtrate decolorized with SO_2. The solution was then evaporated to dryness under reduced pressure. The residue was washed several times with ether, then dissolved in absolute alcohol and finally saturated with CO_2. The precipitated salt was filtered off. On the addition of ether to the filtrate, the potassium sulphonate separated in an amorphous form. It was crystallized twice from water."

The method employed by Reychler[2] is essentially the same as that used by Levene and Mikeska. However, Reychler has given more attention to the details of the procedure. Reychler treated the yield of mercaptan formed from the reaction o

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[1] J. Bio. Chem. 65, 515-518 (1925)
[2] Bull. Soc. Chim. Belge, 27, 110-130 (1913)

50 grams of $C_{16}H_{33}I$ with Na_2S (4 grams of sodium, H_2S in excess, in 160 grams of C_2H_5OH) with a warmed solution of $KMnO_4$ in about 800 grams of water. In order to avoid a too violent reaction, vigorous boiling, foaming, and possible breaking of flask, the temperature of the experiment was kept slightly below 100° C. and the oxidizing agent was added in three or four successive portions. After the mixture was stirred, it was warmed for some time on a water bath. The final reduction of the $KMnO_4$ was accomplished by the addition of oxalic acid. The solution was filtered while warm and the manganese dioxide washed with warm water.

The acid in this procedure was extracted as the lead salt.

CALCULATIONS

Calculations involved in the following laboratory procedures.

From the experiment of Levene and Mikeska, it was found that two mols of potassium permanganate were needed to oxidize one mol of methyl phenyl mercapto methane. This is in agreement with the amounts, in grams, of the materials used.

$$2\ KMnO_4 + HOH \longrightarrow 2\ MnO_2 + 2\ KOH + 3\ (O)$$

$$C_6H_5\text{-}\underset{\displaystyle H}{\overset{\displaystyle SH}{\overset{|}{\underset{|}{C}}}}\text{-}CH_3 + 3(O) \longrightarrow C_6H_5\text{-}\underset{\displaystyle H}{\overset{\displaystyle SO_3H}{\overset{|}{\underset{|}{C}}}}\text{-}CH_3$$

7 grams of methyl phenyl mercapto methane were oxidized by 16.1 grams of potassium permanganate.

Molecular weight of $C_6H_5\text{-}\underset{\displaystyle H}{\overset{\displaystyle SH}{\overset{|}{\underset{|}{C}}}}\text{-}CH_3$ = 138.18

" " " $KMnO_4$ = 158.03

$$\frac{7}{138.18} = \frac{x}{158.03}$$

$x = 8.005$ grams = 1 mol of $KMnO_4$

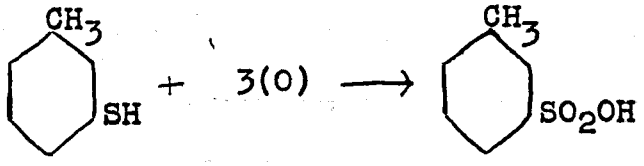
$8.005 \times 2 = 16.01$ grams = 2 mols of $KMnO_4$

From the equation involved in the oxidation of meta-thiocresol to meta-sulpho-benzoic acid, the number of mols of

potassium permanganate needed can be found.

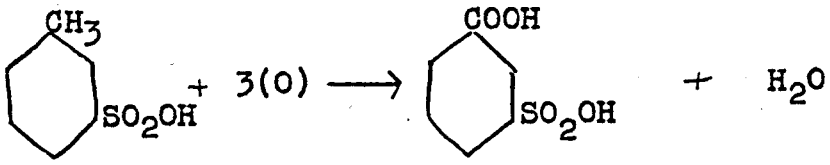
I. The oxidation of the mercapto group.

$$2\ KMnO_4 + HOH \longrightarrow 2\ MnO_2 + 2\ KOH + 3(O)$$



II. The oxidation of the methyl group.

$$2\ KMnO_4 + HOH \longrightarrow 2\ MnO_2 + 2\ KOH + 3(O)$$



Therefore, four mols of potassium permanganate are necessary in order to oxidize one mol of meta-thiocresol.

Hence taking one-tenth of the molecular weight of meta-thiocresol (124.12) as the grams of mercaptan to be used, one may calculate the amount of potassium permanganate needed.

$$\frac{12.4}{124.12} = \frac{x}{158.03} \qquad x = 15.8 = 1 \text{ mol } KMnO_4$$

But 4 mols of $KMnO_4$ as shown by the equation are necessary. Therefore 15.8 x 4 = 63.2 grams of $KMnO_4$ needed to oxidize 12.4 grams of meta-thiocresol.

It was decided to use 12.5 cc. of acetone and 15 cc.

of water as the solvent for the mercaptan and 300 cc. of acetone as the solvent for the permanganate which is to be first dissolved in water (the quantity of which may be increased if necessary) before adding the acetone.

As meta-thiocresol is a liquid it facilitates matters to measure it in a graduate rather than weighing it. Hence in terms of cubic centimeters 12.4 grams of the mercaptan are equivalent to 11.8 cc.

Specific gravity of meta-thiocresol $= 1.052^{20}$

Therefore $\frac{12.4}{1.052} = 11.8$ cc

LABORATORY EXPERIMENTS IN DETERMINATION OF PROPER OXIDIZING AGENT

It was deemed advisable to test the oxidizing powers of several oxidizing agents, observing their efficiency as to rapidity with and without heat, in case the anticipated oxidation by means of $KMnO_4$ was not obtained.

I. Nitric Acid (concentrated).

10 drops of meta-thiocresol were treated with 20 drops of conc. HNO_3 and 10 drops of H_2O. As the HNO_3 was added, a very vigorous reaction took place, fumes of the oxides of nitrogen being copiously evolved. When the H_2O was added, a yellow precipitate formed and a brown substance which, on the continued addition of the conc. HNO_3, settled out on top as an oil. The mixture was refluxed for fifteen minutes. On heating, the precipitate dissolved, but the oil remained insoluble. On cooling, the mixture regained its original characteristics. It was diluted with water and evaporated to dryness. This was repeated until all the oxides of nitrogen were removed. $CaCO_3$ in excess, was added to the aqueous solution of the mixture. A slight clouding occurred, but on excessive addition of $CaCO_3$ it disappeared. The mixture was heated to boiling. The oil remained in the solution.

The violent reaction with nitric acid makes the use of this oxidizing agent inadvisable.

II. Nitric Acid (dilute).

20 drops of meta-thiocresol treated with 30 drops of dilute HNO_3. No reaction took place but on heating a most vigorous one occurred. A brown oil and yellow precipitate formed and fumes of nitric oxides came off profusely.

On refluxing the brown oil settled to the bottom of the tube and increased in quantity as the yellow precipitate decreased in size, faded in color and finally disappeared.

Part of the liquid on top of the oil was decanted off, and to it was added conc. HNO_3 drop by drop. No reaction took place.

To the rest of the mixture conc. HNO_3 was added, heating and stirring, the mixture. The oil remained unchanged.

After filtering off the oil, a portion of the liquid was neutralized by NH_4OH, evaporated to dryness and heated to drive off the NH_4OH. This was not a successful method of extraction, as the entire solid decomposed on heating.

To another portion of the liquid $Ba(NO_3)_2$ was added drop by drop. A white crystalline precipitate was slowly formed. The solid was washed several times with H_2O which was tested for the presence of the nitrate in order to be sure complete precipitation occurred. This solid was thought to be the barium salt of meta-sulpho-benzoic acid and was tested to prove the absence of the nitrate as follows:-

(a) Ferrous sulphate and conc. H_2SO_4 added to an aqueous solution of the solid. A white precipitate formed, the lower

part of which became purple in color. There was no brown ring which is the indication of the presence of a nitrate.

(b) Metallic copper and conc. H_2SO_4 were added to the solid and the mixture heated. The characteristic blue color which indicates the presence of a nitrate (HNO_3 liberated during the reaction acts on copper to form a blue color) did not appear.

These experiments show that oxidation did take place using dilute HNO_3 as an oxidizing agent in that the solid formed during the reaction was not a nitrate and was presumed to be the barium salt of the sulphonic acid. However no reaction took place until the solution of the mercaptan and the dilute HNO_3 was heated and then a very vigorous one. This again renders the use of dil. HNO_3 inadvisable.

III. Hydrogen Peroxide.

A. 3 % solution - 5 drops of meta-thiocresol were treated with 10 drops of H_2O_2. The reaction took place very slowly - no heat being generated and an extremely small white precipitate formed.

B. 30 % solution - 8 drops of meta-thiocresol were treated with 40 drops of superoxol. White precipitate formed but no heat evolved. Reaction very slow.

The above procedures were repeated using MnO_2 as a catalyst. The results were as follows:-

When added to -

A. No noticeable change took place.

B. Fairly vigorous reaction occurred.

(Note:- MnO_2 was prepared by heating it in a crucible at red heat for several minutes to remove any organic material present.)

In all the cases described using hydrogen peroxide, there were always two layers, H_2O_2 and the mercaptan which remained despite the slight reaction, even when the MnO_2 was used.

IV. Sodium Dichromate.

1 cc. of meta-thiocresol suspended in 3 cc. of H_2O were treated with approximately 1 gram of sodium dichromate and 2 cc. of dilute H_2SO_4. No noticeable reaction took place. The solution was diluted with 15 cc. of H_2O and boiled under reflux for 1 hour. A yellow oily solid formed as did a red solid. These were removed by filtration and the filtrate, a deep brown solution, evaporated to dryness; a hard charred mass resulted. This yellow oil possessed the same odor as the meta-thiocresol and was assumed to be the mercaptan.

Since the greater part of the mercaptan was not acted upon by the sodium dichromate, this oxidizing agent was not considered efficient.

PREPARATION OF M-SULPHO-BENZOIC ACID

I. A. Oxidation of Mercaptan.by $KMnO_4$ in Acetone Solution.

11.5 cc. of meta-thiocresol were dissolved in 12.5 cc. of acetone (with no noticeable change, acetone acting purely as a solvent). This solution was placed in a round bottom flask (2 liters) and a solution of potassium permanganate in acetone was slowly added (concentration of $KMnO_4$ was 63.2 grams per 60 cc. acetone and 300 cc. of water). There was no heat generated after the addition of the oxidizing agent. However a dark brown precipitate formed in the flask and this same reaction took place in the flask containing the potassium permanganate solution. It consumed one to one and a half hours to run in the greater part of the oxidizing solution. It was noticed that when heat was applied that the contents of the flask vaporized (evidently this was the acetone), at a very low temperature. The remaining portion of the $KMnO_4$ was added while the flask was heated over a water bath. The contents of the flask were filtered and the filtrate (90 %) was clear yellow in color (10 % being cloudy white in appearance and an oily substance settling out).

To insure the complete oxidation of meta-thiocresol the $KMnO_4$ solution was added to the filtrate. Again a brown precipitate formed in the flask. This process was repeated 8 times (filtering with suction and adding the $KMnO_4$). Heat was applied after each addition of the $KMnO_4$ sol. 890 cc. of

$KMnO_4$ sol. were added and the mixture continued to decolorize the $KMnO_4$ sol (the permanency of the purple color is the indication of complete oxidation). After the final portion of $KMnO_4$ sol. was added, the mixture was refluxed for 1½ hours (using a water bath) and filtered twice, first through a Buchner funnel (1 liter) and then through a glass funnel containing 2 filter papers. 4 cc. of the $KMnO_4$ sol. were added to the filtrate and the mixture was refluxed for 20 minutes. The solution became decolorized.

This procedure was repeated as follows:

50 cc. $KMnO_4$ sol. added; refluxed 65 minutes; solution decolorized; filter.

150 cc. $KMnO_4$ sol. added; refluxed 15 minutes; solution decolorized; filter.

375 cc. $KMnO_4$ sol. added; refluxed 60 minutes; solution decolerized; filter.

At this point, in order to continue experimental investigation, it was assumed that the mercaptan was completely oxidized in view of the fact that more than the calculated amount of $KMnO_4$ had been added. The mixture was filtered and the filtrate, a clear yellow liquid was evaporated under reduced pressure over a water bath.

B. Removal of Acetone.

The acetone was removed by distillation, the temperature of the solution distilling over was about 58° C. When most of the acetone was removed, suction was again applied.

At 87°C. the liquid distilled over. The water bath was removed and the distillation continued.

(Note:- Caution was observed as it was probable that traces of acetone remained in the solution.)

The reduction in pressure was accomplished by the water pump.

C. Evaporation.

In order to prevent any decomposition of any solid present due to direct heating, the solution when about ¼ of its original volume, was poured into an evaporating dish and evaporated to dryness over a water bath.

As the solution became more concentrated, the yellow color deepened to a reddish brown hue. The resulting solid was extremely deliquescent and dried in a desiccator over night. It was assumed that this solid consisted mainly of the potassium salt of meta-sulpho-benzoic acid contaminated by inorganic salts. The weight of the solid produced was approximately 7 grams.

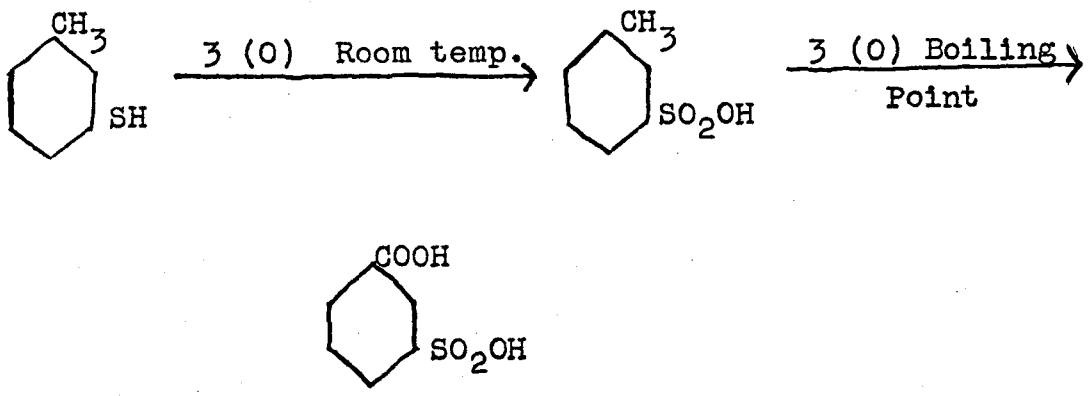
D. Theory of Oxidation.

Since the SH group is so readily oxidized, it was thought that this reaction took place at room temperature, while heat was necessary to oxidize the CH_3 group.

The chemical changes involved in this procedure may be briefly summarized as follows:

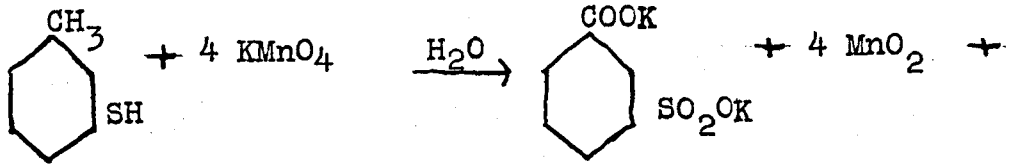
(1) $4\ KMnO_4 + 2\ H_2O \longrightarrow 4\ MnO_2 + 4\ KOH + 6\ (O)$

(2)



or

(3)



2 KOH + H_2O

EXTRACTION OF META-SULPHO-BENZOIC ACID

As meta-sulpho-benzoic acid is soluble in most of the common solvents, water, ether and alcohol, the extraction of this acid presents an interesting problem to be solved.

The following methods of extraction were employed:-

A. Aqueous Solution of Metallic Salts.

In an effort to extract meta-sulpho-benzoic acid from its potassium salt, several metallic salts (in solution) were used. It was hoped to precipitate an insoluble metallic salt of meta-sulpho-benzoic acid.

(1) A small portion of the dried solid was dissolved in water. A slight turbidity resulted in the solution which did not dissolve when heated. After several filtrations this turbidity remained and to the solution was added a 10% solution of $CuSO_4$. There was no visible change in the solution.

Another portion of the solid was dissolved in water and to the solution (without heating or filtering) the copper sulphate solution was added directly. A precipitate resulted; it appeared to be whiter and flakier than the particles causing the turbidity in the aqueous solution. This solution was filtered and the residue was washed 12 times with cold water to remove any excess $CuSO_4$ present. The residue (assumed to be in part the copper salt of the acid) was suspended in water and into it was run H_2S. If the acid was present, it was

thought that the copper sulphide would be precipitated and the acid would be in the aqueous solution. No positive results were obtained (CuS did not precipitate).

(2) The procedure followed in using the metals listed below is:- a small amount ($\frac{1}{2}$ gram) of the potassium salt of meta-sulpho-benzoic acid was dissolved in water and the metallic solution added drop by drop. To this was added a few drops of dilute HNO_3. The metallic solutions and the size of the precipitates resulting from their addition are listed as follows:

(a) $ZnSO_4$ (100 %) - fairly profuse precipitate.

(b) $Pb(NO_3)_2$ - small precipitate.

(c) $MgCl_2$ - no appreciable precipitate.

(d) $CaCl_2$ (10 %) - no " "

(e) $HgCl_2$ (10 %) - " " "

(f) $HgNO_3$ (10 %) - " " "

(g) $FeCl_3$ (10 %) - " " "

(h) $AgNO_3$ (5 %) - fairly profuse "

(i) $Ba(NO_3)_2$ (10 %) - large "

(j) $Bi(NO_3)_2$ - fairly large precipitate formed upon the addition of the first few drops of $Bi(NO_3)_2$ but this was slightly dissolved by the addition of more $Bi(NO_3)_2$.

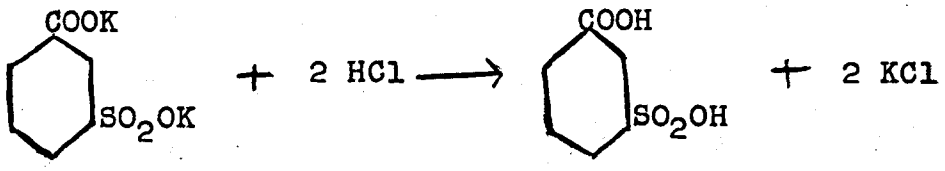
All these precipitates excepting the silver one disappeared in the presence of HNO_3. This showed that they were probably only hydroxides and not the salts of meta-sulpho-benzoic acid. The

silver precipitate did not dissolve in an excess of HNO_3. The solution was filtered and the residue washed several times with water. It was suspended in water and saturated with H_2S; the silver sulphide did not precipitate.

Since it was desired to produce a metallic sulfonate insoluble in a slightly acidic medium, these procedures were regarded as inadvisable.

B. Dry Hydrogen Chloride.

I. 4 grams of the potassium salt of m-C_6H_4(COOH)(SO_2OH) dried in a desiccator for several days were suspended in dibutyl ether and saturated with dry hydrogen chloride. A mechanical stirrer kept the particles in constant agitation and prevented their settling at the bottom of the flask. (See apparatus p. 42) The solid which was brown in color became white. It is hoped that this procedure will remove the potassium from the acid as KCl and liberate the acid.



A small amount of the solid, despite the constant stirring settled at the bottom of the flask. 5 cc. of water were added to bring it into suspension again.

(Note:- Since the solid salt absorbed moisture so readily, it should be triturated and returned to desiccator to dry and then transferred very rapidly to the reaction flask.)

(It is necessary that the solid be finely powdered and entirely to remain suspended in the ether solution.) In both the aqueous and ether layers, an oily substance appeared as the HCl saturation was continued.

The results of this experiment were kept for several weeks in a stoppered bottle. During this interval, the stopper was dislodged. An examination of the mixture showed that (a) considerable evaporation had occurred; (b) more oil had settled out in the mixture; (c) the precipitate had become more dense; (d) a distinct odor of HCl was present.

The mixture, the oil and solid substance, was evaporated to dryness under reduced pressure and over a water bath. The residue, a brown amorphous mass was suspended in ether and the mixture heated to boiling over a water bath. The whole mass seemed to dissolve as the liquid became deep brown in color. On cooling a white crystalline solid separated out at the bottom of the ether solution. The mixture was filtered.

(a) White crystalline solid - washed several times with ether and this wash ether added to the filtrate.

(1) The crystals were extremely soluble in water.

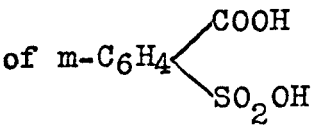
(2) After washing crystals several times with water a few were dissolved in water and to this solution was added $AgNO_3$. A precipitate formed denoting the presence of a chloride.

(3) An aqueous solution of the crystals was treated with an aqueous solution of sodium cobalti-nitrite. A yellow precipitate formed denoting presence of potassium.

Therefore, the white crystalline solid was thought to be KCl.

(b) The filtrate - evaporated to dryness over water , a dark brown oil formed. This oil had a piercing pungent odor. The oil did not solidify when cooled in an ice bath.

(1) As dibutyl ether has been successfully used to isolate sulphonic acids, it was decided to try to crystallize the oil from this solvent. This was hot successful and after evaporation of ether, the oil formed.

II. Another attempt was made to extract the meta-sulphobenzoic acid by HCl saturation. 4 grams of the potassium salt of  were suspended in 50 cc. of normal butyl ether and 50 cc. water. HCl was run into the mixture which was constantly stirred. For 3 hours the HCl bubbled into the ether suspension. An oily substance settled out on the ether

layer; a fine white solid appeared in the aqueous layer together with a small amount of oil. During the saturation the solution became hot. After a total of 8½ hours, the reaction was considered complete.

(a) The two layers were separated. The white solid in the aqueous layer dissolved upon the addition of more water.

(b) The ether layer was clear yellow in color. It was evaporated over a water bath to ½ its volume. During this evaporation a dark brown solid separated out and the remaining liquid was distilled off under reduced pressure between 90-110°C. The residue appeared to be a dark brown oil. There was found in the oil, after standing several days, a few white crystals. The mixture was treated with water to separate the crystals from the oil which was not soluble in water and filtered through a wet funnel. The aqueous solution was evaporated to dryness; the residue was a yellow scum in the center of which clustered a few crystals.

A melting point of the crystals (impure) was taken and found to be between 141 - 143°C.

The melting point of m-$C_6H_4\begin{cases}COOH\\SO_2OH\end{cases}$ is 141°C.

II. Oxidation of Mercaptan by $KMnO_4$ in purified Acetone Solution.

Due to the fact that the acetone, used in the previous preparation, contained oxidizable material, it was necessary to use an excessive amount of $KMnO_4$. In order to remove these impurities, it was decided to distill the acetone several times over $KMnO_4$ after the method of Sachs.[1]

It was decided to prepare the acid on a smaller scale using the purified acetone.

2 grams of meta-thiocresol were dissolved in 20.16 cc. of acetone and 2 cc. of water. A solution of $KMnO_4$ (10.1 gm. in 96 cc. of acetone and 48 cc. water; see calculations p.35) was added to the m-thiocresol - a mechanical stirrer keeping the mixture in agitation. The mixture was refluxed for 2 hours and MnO_2 formed was filtered off. The filtrate was a yellow cloudy liquid. Again, it was decided in view of the amount of $KMnO_4$ used and in order to continue experimental investigation, to consider oxidation complete.

On standing for 2 hours before removal of acetone, the color of the solution changed to a deep orange. The acetone was removed as before and the solution evaporated to dryness. A dark brown solid separated out. This solid was extremely deliquescent and similar to the solid obtained before (I A).

The residue was finely powdered and placed in a

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[1] Lassar Cohn, Arbeits Methoden Für Organische Chemische Laboratorien, p. 711

desiccator for 2 days. It was suspended in 75 cc. of ether and saturated with HCl according to the usual method. The suspended solid became white in color and the ether became yellow. An oil settled out on the ether layer which was decanted from the solid.

More ether was added to the ether decantation in an effort to dissolve the oil. The mixture was heated on a water bath and the oil still remained insoluble. The mixture was evaporated to a few cc. and cooled in an ice bath in an attempt to crystallize out the oil. This was not successful, and the last of the ether was removed by evaporation. A dark brown oil with a piercing pungent odor remained. It was insoluble in water and did not solidify after standing in a desiccator for 10 days.

It is peculiar to note that in only one attempt out of three were white crystals found as the final product and these in no appreciable amount. In the other two cases, a dark brown oil formed and yet each extraction was similar to the other.

III Oxidation of Mercaptan by $KMnO_4$ in Aqueous Solution.

In the previous preparations, it will be recalled that acetone was the solvent for the mercaptan and the $KMnO_4$. Since these preparations can not be termed successful, it was decided to repeat the procedure using water as a solvent.

A test was made to determine the qualities of water as a solvent, 1 cc. of m-C_6H_4(SH)(CH$_3$) in 2 cc. of water was treated with 2 cc. of an aqueous solution of $KMnO_4$. An immediate reaction took place as indicated by the MnO_2 which was instantly precipitated. An additional amount of $KMnO_4$ was needed to complete the oxidation. However, the efficiency of water as a solvent was proved by the instantaneous reaction.

To 12.4 grams of m-thiocresol in 125 cc. of water was added an aqueous solution of $KMnO_4$ (40 gm. $KMnO_4$ in 700 cc. of water. This is in excess of the calculated amount of $KMnO_4$ - see Calculations p. 35).

The $KMnO_4$ solution was prepared by dissolving the solid $KMnO_4$ in cold water in which it did not readily dissolve. The mixture was heated and the $KMnO_4$ finally dissolved. The solution was cooled before adding to the mercaptan.

During the addition of the $KMnO_4$ solution which was added in small portions to the mercaptan, the mixture was constantly agitated by the mechanical stirrer. A little heat was generated. After the final addition of the $KMnO_4$, the

mixture was allowed to stand over night. MnO_2 formed was not filtered, because of the presence of a white oily suspension which adhered to part of the MnO_2 and floated on the surface of the liquid. There was also some $KMnO_4$ which had settled at the bottom of the reaction flask. To dissolve this, 775 cc. of water were needed. At this point the oily suspension had disappeared and the mixture was allowed to stand over night and the solution retained its purple color. The MnO_2 was removed by filtration through a Buchner funnel.

It was hoped that this cold treatment of the mercaptan by $KMnO_4$ would easily convert the mercapto group to the sulphonic group and that by the addition of further $KMnO_4$ and by heating, to oxidize the methyl group.

700 cc. of aqueous $KMnO_4$ solution (40 gm. $KMnO_4$) were now added to the filtrate in small portions. The solution was allowed to reflux for 1 hour -- no visible change took place. The mixture was refluxed for approximately 60 hours. It was filtered occasionally during this time but the size of the precipitate in each case warranted the belief that oxidation was taking place very slowly. The solution bumped very violently when heated over an open flame. To avoid this, it was refluxed for a time over an oil bath containing liquid paraffin. (Flash point 180°C. -- as a precaution the temperature was kept at 120°C.)

This method of refluxing was too slow and did not stop the bumping. Sand, pumice and glass beads did not help.

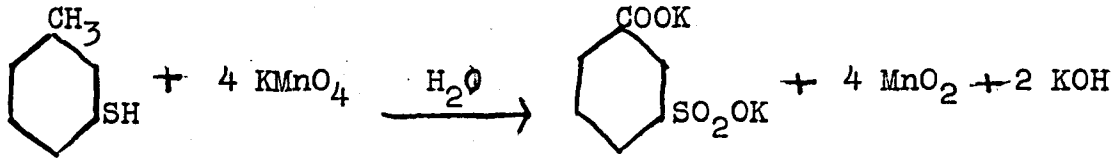
Finally, the solution was divided into 2 parts and it was found that by the proper adjustment of the flame the bumping could be avoided.

It was decided to test the solution after filtering off MnO_2 to find just how much oxidation had taken place. in view of the fact that an excess of 16.8 grams of $KMnO_4$ had been added and the solution refluxed for 60 hours.

200cc. of the solution was withdrawn and treated as follows:

200 cc. decolorized by SO_2, precipitate formed, removed by filtering. The filtrate was saturated with HCl and evaporated in the hood to dryness. The following equations show the possible compounds present in the residue.

(1) Oxidation of Mercaptan.



$+ H_2O$ and $KMnO_4$ in excess.

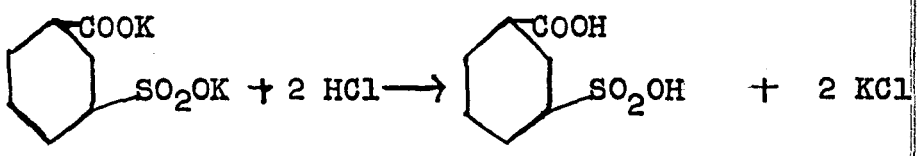
(2) Decolorization with SO_2, removal of $KMnO_4$ in excess.

$$H_2O + SO_2 \longrightarrow H_2SO_3$$

(a) $2\ KMnO_4 + 5\ H_2SO_3 = K_2SO_4 + 2\ MnSO_4 + 2\ H_2SO_4 + 3\ H_2O$

(3) Saturation with HCl.

(a)



These equations show that in the residue in addition to the meta-sulpho-benzoic acid, there are chlorides and sulphates.

The residue was analyzed as follows:

(1) Test for Organic Material -- slightly affirmative.

(a) Heated few grains of solid on rod -- material became partly charred.

(b) When treated with H_2SO_4 the solid became brown.

(2) Tests for chloride and sulphate -- affirmative.

(a) Aqueous solution of solid with $AgNO_3$ gave a precipitate indicating presence of chloride.

(b) Aqueous solution of solid with $BaCl_2$ gave a precipitate indicating presence of sulphate.

(3) Test for potassium affirmative -- flame violet.

This analysis shows that the solid obtained on evaporation was a mixture of chlorides and sulphates with a slight amount of organic matter present.

OXIDATION IN BASIC AND ACIDIC MEDIUMS

In view of the facts presented, it was thought that oxidation was not complete. Since the value of an organic synthesis lies partly in the ease and the rapidity with which it may be accomplished, it was decided that the time consumed in the oxidation was much too long. By making the solution acidic or alkaline, the oxidation may be hastened. This was experimented upon with the following results:-

A:- A portion of the original solution, approximately 400 cc., was placed in a flask and to this was added 50 cc. of 10 % sodium hydroxide. The solution was refluxed approximately 4 hours daily for about a week. No visible change was noticed and much bumping accompanied the refluxing. This treatment was deemed valueless.

B:- 400 cc. of the original solution were treated with 50 cc. of dilute sulphuric acid and refluxed for several hours. In comparison to the alkaline solution, the bumping was negligible and was finally avoided by proper adjustment of the flame. A large precipitate of MnO_2 resulted from the refluxing and was filtered off. This MnO_2 precipitate was black while other precipitates of MnO_2 were chocolate brown in color. After several hours more of refluxing, the solution became colorless, showing that the $KMnO_4$ solution was completely reduced. As the oxidation of the mercaptan was not complete (end-point being the permanency of the purple color of the

$KMnO_4$), more potassium permanganate solution was added (20 gm. $KMnO_4$ in 350 cc. hot water). The solution was refluxed for 52 hours. At this point, the purple color still remained and the oxidation was considered complete, although a very small precipitate of MnO_2 continued to form.

The amount of potassium permanganate used to obtain these results was approximately 100 grams and the time comsumed in refluxing was about 112 hours.

(Note:- The addition of the $KMnO_4$ solution in small portions (50 cc., 25 cc., 20 cc., 10.cc., 5 cc.,) causes the end point to be reached easily and avoids at this point a too great excess of $KMnO_4$.)

Since the use of hydrogen chloride gas was not especially successful in former experiments, it was decided to follow a method analogous to the one used by Levene and Mikeska.[1]

I. 100 cc. portion of the oxidized solution was decolorized by sulfur dioxide and evaporated to dryness. A solid quite large in quantity settled out on evaporation which was completed over a water bath. The following tests were made on the solid:

A. (1) A distinct odor of sulphur dioxide was evolved from the solid when a part of it was heated over a direct flame.

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[1] J. Biol. Chem. 65 (515-18) 1925

(2) The presence of the sulphate radical was shown by adding $BaCl_2$ to an aqueous solution of the solid acidified by HNO_3. A white precipitate formed which did not dissolve in an excess of HNO_3 and H_2O.

(3) The presence of organic material was shown by treating a part of the solid with concentrated sulphuric acid. A part of the solid became charred.

B. The solid was washed several times with ether, dried, and following the procedure of Levene and Mikeska treated with absolute alcohol. A very small part of the solid dissolved in the alcohol -- as shown by the gray coloring which appeared in the alcohol. The greater part of the solid remained undissolved and was separated from the liquid by decanting the alcohol.

(1) In an effort to dry this solid, it was placed in an evaporating dish and heated over a water bath. A part of the white solid decomposed forming an oily material.

(2) The alcohol from the decantation was evaporated to dryness, a gray oil separating out, but on further concentration, it changed to a dark brown oil.

(a) A few drops of this oil were treated with aniline, a white precipitate formed. This was proved to be aniline sulphate, showing that the oil was partially composed of a sulphate; by suspending the oil in water, heating the

mixture to boiling and finally filtering the solution and treating the filtrate with $BaCl_2$. The white precipitate formed showed the presence of a sulphate.

(b) An attempt was made to purify the oil by distillation, this was unsuccessful due to the small quantity of oil extracted.

The investigator did not follow any further the procedure of Levene, namely, saturating the alcoholic extraction with carbon dioxide, since the experiments just listed indicate that the alcohol extracted very little of the organic material.

II. Since alcohol extracted so little of the organic acid, it was decided to use ether instead.

A. 100 cc. portion of the oxidized solution obtained from oxidation of m-thiocresol by $KMnO_4$ (p. 59) was decolorized with alcohol instead of SO_2. The decolorized solution was evaporated to dryness and acidified with dilute H_2SO_4. This acidic solution was intimately shaken with ethyl ether. The ether layer was separated and evaporated to dryness. An oily substance resulted which, when cooled in an ice bath, crystallized in a needle like mass. These crystals were extremely deliquescent, and were not dried after several days in a desiccator.

The aqueous acidic layer was again shaken with ether and the ether layer evaporated to dryness. This was

repeated several times. The residue resulting from the ether evaporation was an oil which could not be crystallized in an ice bath with constant rubbing of glass rod to side of beaker to aid the crystallization.

B. 400 cc. of the oxidized solution were decolorized with alcohol and evaporated to dryness. This residue was acidified and the solution shaken with ether. The ether layer was separated and the aqueous acidic layer again shaken with ether. This process was repeated 6 times. The combined ether layers were evaporated to dryness. An oil resulted which, when cooled suddenly in an ice bath, became crystallized; a liquid also formed. This liquid could not be removed by heating on a water bath, drying in a desiccator and electric oven. The crystals seemed to be a mixture of needle and rhombic crystals.

(1) A few of the crystals were dissolved in water and treated with $BaCl_2$. A white precipitate formed. This indicates the presence of a sulphate.

(2) A few of the crystals in aqueous solution were tested with sodium cobalti-nitrite. The yellow precipitate which indicates the presence of potassium did not appear.

It was thought that these crystals were K_2SO_4 which separated out from the ether (which was not anhydrous).

(3) These crystals did not redissolve in ethyl or dibutyl ether even when the ether solutions were heated.

(4) These crystals could not be melted when heated to 200 C.

C. 100 cc. portion was treated in the usual manner. The ether layer was evaporated. A brown oil and a white solid remained. This residue was evaporated further over an open flame. It decomposed at a low temperature -- a very large carbon deposit resulted. This seemed to indicate that the ether extract is of organic nature.

It is interesting to note that the final product, (obtained from evaporated ether extract), either oil or crystals, possessed the same odor -- a sweet pleasant aroma.

The investigator decided to test the powers of benzene as an extracting agent.

100 cc. portion of the oxidized solution was evaporated and acidified as before. The solution was intimately shaken with benzene. The benzene layer was separated and evaporated almost to dryness. The remaining solution was cooled in an ice bath. A few small white crystals separated out. Such a minute quantity that they were hardly perceptible.

IV. Oxidation of Mercaptan by $KMnO_4$ in Aqueous Solution.

I. Another attempt was made to prepare meta-sulpho-benzoic acid.

The calulated amount of the mercaptan (12.4 gm.) was treated with $KMnO_4$ solution (40 gm. in 700 cc. H_2O) with constant stirring. The solution was made acidic and the purple color disappeared. 700 cc. more of $KMnO_4$ were added (40 gm. $KMnO_4$) and the mixture refluxed for 10 hours. At this point, the characteristic odor of $C_6H_4\diagdown\!\!\begin{matrix}CH_3\\SH\end{matrix}$ was very strong and the $KMnO_4$ solution retained its color.

The liquid was divided into 2 equal portions (to facilitate matters). After refluxing for 2 hours more, the solutions were found to be neutral. To each, 50 cc. dilute H_2SO_4 were added. It was noticed that some of the $KMnO_4$ had settled at the bottom of the flasks as a solid. To dissolve this 250 cc. H_2O were added to each flask. The solutions stood for a week and during this time, they became decolorized. 25 cc. $KMnO_4$ were added to each.

The investigator decided to allow one portion to stand at room temperature, adding $KMnO_4$ in small amounts to make, if possible, a comparison of the rate of oxidation with and without heat. This sample was not completely oxidized after 7 weeks at room temperature -- an excess of $KMnO_4$ solution being added.

The other portion was treated as formerly. The $KMnO_4$

solution added in small amounts, the solution refluxed, filtered and this procedure repeated. This was continued for approximately 100 hours (during 5 weeks) with an excess of approximately 24 grams $KMnO_4$ (in solution) added.

(Note:- In an effort to determine the purity of the mercaptan used, a ten cc. sample was distilled. The boiling point of $C_6H_4\begin{matrix}-CH_3\\ \diagdown\\ SH\end{matrix}$ varies, in literature, 194.5 - 200°C; approximately 9 cc. of the meta-thiocresol distilled over at 189°C and 1 cc. at 192°C.)

The oxidation was still not complete as shown by the decolorization of the solution. Here again, in order to continue experimental analyses, the oxidation was considered complete.

A. 100 cc. portion (acidic) was treated with $CaCl_2$ solution (50 %); a precipitate of $CaSO_4$ immediately formed. When no further precipitation took place, the mixture was filtered and heated, but no more $CaSO_4$ formed. The filtrate was evaporated to dryness, a white solid presumably the calcium salt of $C_6H_4\begin{matrix}-COOH\\ \diagdown\\ SO_2OH\end{matrix}$ remained contaminated by some $CaSO_4$. This was treated as follows:

(1) A few grains of the solid were dissolved in water and the solution neutralized with conc. H_2SO_4. $CaSO_4$ precipitated and was filtered off. The filtrate was evaporated over a low flame. The greater part of the solid settling out became immediately charred, while the rest was a white solid similar to $CaSO_4$.

2. A small amount of the solid (obtained from A) was dissolved in H_2O and dilute H_2SO_4 was added until precipitation no longer occurred. After filtering and standing over night, the filtrate, still clear, was evaporated to $\frac{1}{2}$ its original volume. On cooling a profuse, white, needle-like mass of crystals separated. The mixture was filtered.

(a) The filtrate was yellow in color possessing a clean antiseptic odor.

(b) The residue was analyzed as follows:

(1) A few grams of residue were placed on a crucible cover and heated. The outside coating of the solid charred, when the charred matter was removed, a white solid remained.

(2) The solid did not melt when heated to 200°C.

(3) An aqueous solution of the solid, colored blue litmus red showing its acidic nature.

(4) The solid was slightly soluble in cold H_2O, completely soluble in hot H_2O, dilute acid and alkali.

(5) An aqueous solution of the solid with $BaCl_2$ gave a white precipitate. This is an indication of the presence of a

sulphate.

Note. The investigator found that an aqueous solution of -toluene sulfonic acid treated with $BaCl_2$ gave, also, a white recipitate.)

(6) An aqueous solution of the solid treated with ammonium oxalate gave a white precipitate. This is an indication of the presence of calcium. When a grain of the solid was held in a flame, the flame became red in color. This is an indication of the presence of calcium.

(7) When fused with KOH, a distinct odor of sulphur dioxide was present. On the addition of bromine water to the mixture, a white precipitate formed. This is an indication of the presence of a phenol, as was also shown by the odor of a phenol which came from the mixture.

(8) A portion of this crystalline mass was treated with dilute H_2SO_4. The acid was added drop by drop until the precipitation of $CaSO_4$ no longer occurred. The mixture was filtered.

(a) A part of the filtrate was evaporated to dryness. It immediately charred.

(b) Another part of the filtrate was evaporated to $\frac{1}{2}$ its original volume.

The liquid was intimately shaken with ethyl ether. When the ether extract was evaporated to dryness, a white oily substance remained. It was impossible to crystallize this substance even when it was cooled to 11° C. below 0° C. This procedure was repeated several times using sometimes isopropyl ether. An oil resulted in each case.

These tests indicate that the white needle-like crystals were the calcium salt of meta-sulpho-benzoic acid. Since further identification of this salt could not be made due to the unsuccessful extraction of the acid, (hence no melting point of the acid itself could be obtained), a derivative was made. The results of this procedure will be recorded later (p. 81).

B. 200 cc. of portion of the oxidized solution (obtained from oxidation of mercaptan, see p. 65) was evaporated to dryness. A white crystalline solid resulted. The investigator tried to extract the meta-sulpho-benzoic acid using the following solvents, ether (ethyl and isopropyl), alcohol (absolute, 95% ethyl), acetone, and benzene. The results were the same in every instance, an oily substance remained when the solvent was removed. This oily matter could not be crystallized.

A similar extraction was made using iso-amyl alcohol. When the alcohol was removed by distillation, a white gelatinous solid remained. This residue on standing became an oily liquid and again partly solidified. The mixture was shaken with ether. A white flaky solid settled at the bottom of the flask. When heated this decomposed between 200°C -220°C.

The residue remaining after the acid had been removed by the solvents was analyzed.

(a) The presence of potassium was indicated by the formation of a yellow precipitate when a portion of the solid was treated with sodium cobalti-nitrite.

(b) The presence of the sulphate radical was shown by the formation of a white precipitate when the solid was treated with $BaCl_2$.

(c) The presence of manganese was shown by the formation of the purple color when the solid in dilute nitric acid was treated with sodium bismuthate.

These tests indicate that the products of the oxidation of meta-thiocresol by $KMnO_4$ (pp. 64, 65) are an organic oily substance, K_2SO_4, $MnSO_4$, and H_2O.

V. Oxidation of Mercaptan by $KMnO_4$, in 5% excess of Calculated Amount, in Aqueous Solution.

Since the previous oxidations of meta-thiocresol by $KMnO_4$ were not successful, in view of the fact that tests and extractions showed very little organic matter present, it was decided that the excessive amounts of the oxidizing agent may have oxidized the mercaptan to a greater extent than desired. This did not seem possible because of the presence of the mercapto group and the ease with which it is oxidized. Hence, it was determined to use in this oxidation of the mercaptan only five percent in excess of the calculated amount of $KMnO_4$ (p.35).

To 11.8 grams of meta-thiocresol in 125 cc. of H_2O were added 33.18 grams of $KMnO_4$ in 580 cc. of H_2O. The oxidizing agent was added in small amounts through a dropping funnel and the mixture was constantly agitated by a mechanical stirrer. The addition of $KMnO_4$ took 1 hour. 50 cc. of dilute H_2SO_4 were added to facilitate the oxidation. A very little heat was generated during the reaction. A large precipitate of MnO_2 was formed and the solution still retained the purple color. The mixture stood for several hours and was filtered. The precipitate of MnO_2 was boiled in 100 cc. of H_2O to remove any of the mercaptan that may have clung to it. This was filtered and the filtrate added to the mother liquid. To this solution, another portion of $KMnO_4$ (33.18 gms. in 580 cc. of H_2O) was slowly added while the mixture was gently heated and

stirred. The mixture was refluxed for 10 hours. At the end of this time, the purple color of the permanganate still was retained. The MnO_2 formed was removed by filtration.

The filtrate was decolorized by a few drops of ethyl alcohol.

A. A 250 cc. portion of this filtrate which was acidic was evaporated to dryness. During this evaporation, a gray oil settled out on the surface of the liquid. The residue was a white solid; some of which became charred. A portion of this residue was intimately shaken with absolute alcohol.

(1) The alcohol layer was analyzed. A turbidity remained in the alcoholic extract even after several filtrations. When the alcohol was removed by evaporation, a white solid remained. This solid was dried in the desiccator for two days.

(a) The solid immediately charred when heated on a crucible cover in flame.

(b) It was impossible to obtain a melting point of the solid, as it decomposed when heated in a capillary in an oil bath.

(c) This solid did not redissolve in cold absolute alcohol and was only partly soluble in hot alcohol. The mixture was boiled with bone-black, filtered and evaporated. The result was a very few grains of a yellowish white solid.

(2) The solid remaining after the alcohol extraction was analyzed.

(a) The solid no longer charred when heated on crucible cover.

(b) The presence of the SO_4 radical was indicated by the white precipitate formed when $BaCl_2$ was added to an aqueous solution of the solid.

(c) The presence of potassium was indicated by the yellow precipitate formed when sodium cobaltinitrite was added to an aqueous solution of the solid.

(d) The test for the presence of manganese with dilute nitric acid and sodium bismuthate was negative. The manganese present in the original mixture was evidently removed as manganous dioxide.

It is evident that the alcohol had removed the organic matter present.

(3) Another part of the solid obtained from evaporation of oxidized solution (A) was shaken with iso-amyl alcohol. The undissolved solid was removed by filtration. The alcohol was distilled off at 127° C. The residue was a black charred mass.

(4) Other portions of the solid (from A) were treated by various solvents, ethyl alcohol, absolute alcohol, ethyl ether and di-isopropyl ether. In

every case, the residue remaining, after the solvent was removed by evaporation, was an oily substance, very small in quantity.

B. A 100 cc. portion of the solution obtained from the oxidation of the meta-thiocresol (p. 70) was neutralized with lead carbonate. The precipitated solids were removed by filtration. The filtrate was evaporated to dryness. A white crystalline solid remained.

(1) This solid became charred, in part, when heated on a crucible cover in flame.

(2) An aqueous solution of this solid was saturated with H_2S. A slight turbidity resulted. The mixture was filtered. The filtrate was carefully evaporated to dryness. A white solid resulted.

(a) This white solid decomposed, in part, above 170°C.

(b) This solid charred and became oily when heated over an open flame.

(c) A test was made for the presence of sulfur[1] as follows: a portion of the solid was fused with sodium. An aqueous solution of this was neutralized with dilute HCl. To this 1 cc. of concentrated HCl was added and the mixture cooled. A few grains of p-amino dimethylaniline hydrochloride were thoroughly mixed with the cooled solution. 1 drop of ferric chloride in HCl was

1 Kamm, Qualitative Organic Analysis, pp. 134-135

next mixed with the solution. The blue color formed indicated the presence of sulfur.

(d) Since this solid did not melt at 141°C., the melting point of meta-sulpho-benzoic acid, the investigator thought that the solid may have been a lead salt. Test for the presence of lead with potassium chromate gave negative results.

These laboratory procedures have shown quite clearly that in the products formed from the oxidation of meta-thio-cresol, there is decidedly some organic matter present. This organic material has been extracted in a few instances as a deliquescent, crystalline solid, and in every other case, as an oil.

Due to the small amounts of the solid extracted, it could not be purified. In taking the melting points of the solids obtained from the different extractions the following results were noticed:

(1) The solid melted between 141-143°C. (p. 50)

(2) The solid decomposed between 200-220°C. (p. 69)

(3) The solid decomposed below 127°C. (p. 72)

(4) The solid decomposed above 170°C. (p. 73)

(Note:- The melting point of meta-sulpho-benzoic acid is 141°C. Many sulphonic acids decompose on heating and have no definite melting points.)

The oil which resulted several times from the various extraction possessed a sweet odor. It was not volatile at room temperature; it charred when heated over an open flame. The small amounts in which the oil was extracted prohibited any analysis of it.

It is significant to note that the derivatives of the organic matter produced from the oxidation of the mercaptan were oils with two exceptions.

PREPARATION OF DERIVATIVES

The sulphonyl chlorides and sulphonyl amides or anilides are very frequently used as derivatives in the identification of organic aryl acids or their salts. This is due, no doubt, to the fact that these compounds are easily prepared and can be isolated as crystalline solids with definite melting points. The chlorides are formed from the reaction of an organic acid or its salt with phosphorus pentachloride or thionyl chloride; the amides are precipitated by the addition of concentrated NH_4OH to a solution of the chloride and the anilide by the addition of aniline.

I

$$RSO_2OH\ (RSO_2ONa) + PCl_5 = RSO_2Cl + POCl_3 + HCl\ (NaCl)$$

$$RSO_2OH\ (RSO_2ONa) + SOCl_2 = RSO_2Cl + SO_2 + HCl\ (NaCl)$$

II

$$RSO_2Cl + 2\ NH_3 = RSO_2NH_2 + NH_4Cl$$

$$RSO_2Cl + 2\ C_6H_5NH_2 = RSO_2NHC_6H_5 + C_6H_5NH_2HCl$$

Remsen and McKee[1] identified ortho-sulpho-benzoic acid by the formation of the chloride. They placed the acid

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[1] Am. Chem. Jour. - 18, 794

potassium salt (75-100 grams) in a dish with 2 moles of PCl_5 and rubbed the mixture with a pestle until the reaction was over. The phosphorus oxychloride was distilled off under reduced pressure (or removed by heating for 3 hours on a water bath). The mass was transfered to a cylinder containing 200-250 cc. of water and washed vigorously by churning. After washing 3 or 4 times, the mass was transfered to an ice solution from which the chloride was extracted.

This preparation of the sulphonyl chloride is essentially like the procedure outlined by Clarke[2] and by Gattermann.[3] Clarke recommends that the sulphonyl chloride be purified by distillation under reduced pressure or recrystallized, when possible, from some "non hydroxylic solvent such as benzene or ligroin". When ether[4] is used as the solvent for the chloride, this compound, on the evaporation of the ether, remains as an oil which must be distilled, under reduced pressure, to avoid decomposition.

Gattermann[5] suggests another method of removing the $POCl_3$; the reaction mixture (obtained from PCl_5 treatment) is poured into cold water and after long standing the $POCl_3$ is converted into phosphoric acid.

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[2] A.T.Clarke, Handbook of Organic Analysis, p. 48

[3] L. Gattermann, The Practical Methods of Organic Chemistry, p. 284

[4] J.B. Cohen, Theoretical Organic Chemistry, p. 432

[5] loc. cit.

Thionyl chloride is often preferred to PCl_5 because of the reaction products. In the former, SO_2 is one of the products and is very easily removed; in the latter, $POCl_3$ is formed and special methods must be taken to remove this compound.

The investigator used the procedure (outlined p. 76) and precipitated the amide by the addition of conc. NH_4OH. The results of the various experiments will be shown.

The method of McElvain[6] was used in the preparation of the anilide derivative of meta-sulpho-benzoic acid. It is as follows:- One gram of the paraffin acid (or its sodium salt) is placed in a small flask with approximately the theoretical amount of thionyl chloride (1 mole). The flask is then heated gently under the reflux condenser for 30 minutes using a water bath. The cooled residue is treated with approximately 2 moles of the aniline dissolved in 30 cc. of benzene and the mixture refluxed for a few minutes. The benzene is transferred to a small separatory funnel and washed with water, dilute acid, dilute alkali, again with water and poured through a small filter paper and evaporated to dryness. The anilide is crystallized from CH_3OH to a constant melting point.

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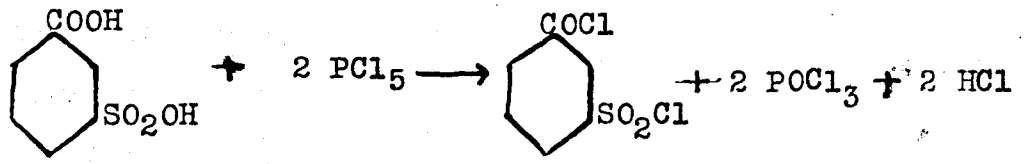
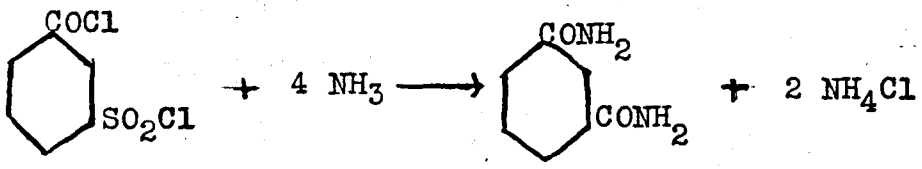
[6] Oliver Kamm, Qualitative Organic Analysis, p. 177; J. Am. Chem. Soc., 53, 1173 (1931)

LABORATORY PROCEDURE

I. The crystals (less than 0.5 gram) obtained from the ether extractions (pp.50,61) were dried as much as possible. To these were added a few grams of PCl_5. A spontaneous reaction took place; a few cc. of a semi-solid was formed. This was heated gently and conc. NH_4OH was added. A fine white precipitate resulted. The excess of NH_3 was driven off. The few crystals and impurities remained. In an effort to recrystallize the solid, from ether, the crystals were lost due to the very small quantity. It was presumed that these crystals were the amide derivative of meta-sulpho-benzoic acid. The following equations show theoretically their formation.





II. A. An attempt was made to prepare a derivative of the acid from its potassium salt (obtained from the evaporation of the decolorized oxidized solution). About one gram of the salt was treated with approximately 1.50 grams of PCl_5 and heated; a vigorous reaction took place. The product was a thick

syrup-like mass. 10 cc. of water were added to dissolve any inorganic salt present. The entire mass dissolved. Upon the addition of the conc. NH_4OH, a very great precipitate was formed. On standing, the solid became pink in color.

(1) It could not be melted up to 300° C.

(2) It was soluble in dilute HCl, insoluble in cold and hot water, alcohol, ether, benzene and dilute KOH.

(3) Tests for sulphur[1] - positive.

Test for nitrogen[2] - negative.

(Note:- 3 tests for nitrogen were made and all were negative.)

(4) Part of the solid was dissolved in dilute HCl and reprecipitated by dilute KOH, a brown flaky solid resulted. When filtered the solid seemed to be oily. An unsuccessful attempt was made to recrystallize the oily substance from ether.

(a) This procedure was repeated. The white precipitate when filtered became a deep brown oil, which was partly volatile.

III. Another derivative was made from the potassium salt of C_6H_4(-COOH, $-SO_2OH$). In this procedure, the $POCl_3$ was distilled off at 107° C. A most vigorous reaction took place when conc. NH_4OH was added to the mixture and a brown amorphous mass formed. To insure the removal of the inorganic salts present, the mass

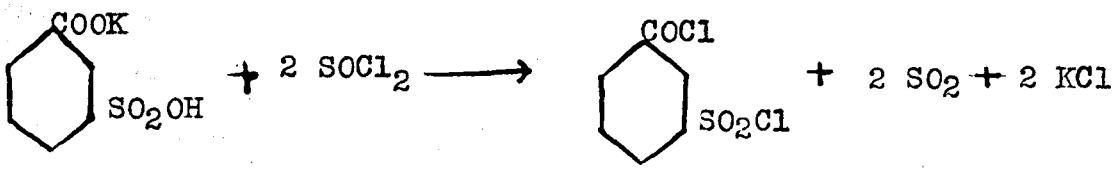
1. Oliver Kamm, Qualitative Organic Analysis, pp. 134-135.
2. Ibid., p. 177

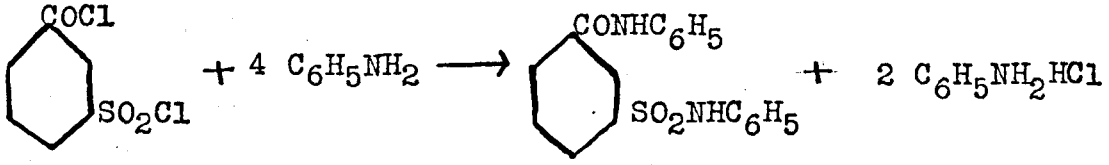
was washed with water; a greater part of the solid dissolved, an oil remained.

(1) The oil was almost wholly soluble in water; soluble in dilute HCl and insoluble in dilute NaOH.

(2) On reprecipitation from HCl treated with NaOH, an oil was formed.

IV. The anilide derivative was prepared according to the method of McElvain. The amounts required were obtained from the equations. 3 grams of the (impure) potassium salt (obtained from evaporating the decolorized oxidized solution prepared in IV. p. 65) were used.





It was difficult to remove the remaining traces of benzene from the aniline. When evaporated to dryness, an oil resulted. Three attempts were made to recrystallize it from methyl alcohol. This was not successful, as an oil still remained.

V. 3 grams of the calcium salt of meta-sulpho-benzoic acid (p. 68) were treated with the calculated amount of $SOCl_2$[1] since benzene had not successfully extracted the anilide

1 Oliver Kamm, Qualitative Organic Analysis, p. 177

derivative, ether was used as a solvent for the aniline. The ether layer containing the anilide was separated and evaporated to dryness; a brown solid resulted. After 3 recrystallizations from methyl alcohol a brownish white solid remained. This solid decomposed when heated above 190°C.

VI. 5 grams of the solid obtained from the oxidation of meta-thiocresol (p.71) were treated with 4.25 grams of $SOCl_2$ [2] and refluxed for 30 minutes. The mixture was cooled and to this were added 3.34 grams of aniline in 30 cc. of di-iso-propyl ether. A part of the mixture, evidently the inorganic matter, did not dissolve in the ether. To this mixture H_2O was added. The solid insoluble in ether dissolved in the water. The ether layer was separated. On standing, there settled out at the bottom of the ether layer a green solid which was quite oily in appearance. This solid could not be removed by filtering, as the mixture decomposed the filter paper. The ether was decanted from the solid which had an extremely pungent odor. The ether layer was evaporated to dryness. An oil which had a very obnoxious odor remained. This oil still remained as such, after several treatments with methyl alcohol.

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2 Ibid.

SUMMARY

In this work the author has presented a complete resumé of the literature concerning the preparation and the properties of meta-sulpho-benzoic acid and a detailed account of the laboratory procedure involved in the synthesis of this acid.

It was the object of the author

(1) to prepare meta-sulpho-benzoic acid from the oxidation of meta-thiocresol by potassium permanganate in the most suitable of various mediums, acetone, aqueous dilute alkaline and dilute acidic. Laboratory data shows that the oxidation in dilute acidic medium was the most rapid.

(2) to separate and extract from the products of oxidation the acid in the free state or as the salt of the acid by some organic solvent.

This synthesis and extraction were not successful. The only organic matter which could be isolated from the oxidation of the mercaptan was an oil. This oil could not be identified because:

(1) It was extracted in very minute quantities.

(2) It defied all efforts of crystallization.

(3) The derivative prepared from the oily organic substance was also an oil.

The investigator believes that in two instances the

salts of the acids were formed, namely, the calcium and lead salts. Tests for the components of these salts uphold this belief. Here, again, the derivative made from the salt (calcium) was an oily substance.

Since it is theoretically possible to oxidize meta-thiocresol to the corresponding sulphonic acid and since it is the usual procedure to extract an organic compound by some organic solvent in which inorganic salts do not dissolve, the author feels that she was justified in her attempts to extract the acid. The analyses of the products of oxidation substantiates this belief.

When a substance capable of being oxidized is treated with potassium permanganate in the presence of dilute sulfuric acid, nascent oxygen is theoretically formed. This oxygen reacts with the oxidizable substance. The decolorization of the potassium permanganate solution and, in some cases, the formation of manganese dioxide are indications that this oxidation is taking place. Both these characteristics were noted during the oxidation of meta-thiocresol by potassium permanganate in acidic medium. An analysis of the by-products of the reaction showed that potassium sulphate, manganous sulphate, water and some oily material were formed. While the oily material was present in the residue of these compounds, the residue charred, in part, on heating. When it was removed by some organic solvent, the residue no longer charred. Hence it seems correct to assume that the oily material was organic

in nature.

This oil does not necessarily have to be meta-sulphobenzoic acid. It is reasonable to suggest that it is a sulphonic acid since the methyl group of meta-thiocresol is oxidized with difficulty while the mercapto group is oxidized with the greatest of ease. Thus, in view of this evidence and in addition to this fact, that sulphonic acids are difficultly crystallized, the oil resulting in this procedure is not a surprising product.

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