

cc. normal sodium acetate was employed. The coefficients of velocity obtained in the two series are given in Table III.

Time. Minutes.	Series No. 1, potas- sium hydroxide.	Series No. 2, normal sodium acetate.
68	0.000141	0.000218
90	0.000141	0.000209
120	0.000156	0.000231
Average	0.000146	0.000219

These results would indicate that at this temperature and dilution, sodium acetate is hydrolyzed to the extent of over one per cent. This number is probably not far from the truth. A more thorough study especially of this last phase of the reaction will soon be undertaken.

STATE COLLEGE OF KENTUCKY,
LEXINGTON, July, 1898.

UPON THE ACTION OF SULPHURIC ACID ON THYMOL.¹

[THIRD PAPER.]

BY JAMES H. STEBBINS.

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MY motive in taking up this subject again, is for the purpose of clearing up certain doubts which had arisen in my mind, in connection with my previous experiments.²

Photomicrographic examinations of the products previously obtained showed so many different forms of crystallization, that I was led to believe that by the treatment of thymol with 66° sulphuric acid, at steam-bath temperature, possibly several isomeric acids are formed.

To gain more light upon this question, therefore the following experiments were made :

Sixty grams of powdered thymol were heated in a beaker on the water-bath, under constant stirring, with fifty grams of 66° sulphuric acid, until the mixture solidified to a crystalline mass, which occurs after nine to ten minutes' heating.

As previously noted, a small quantity of a clear, oily-looking liquid separates, on pressing, from the crystalline cake. This, on being poured off into a beaker, solidifies on cooling to a mass of minute white needles.

¹ Read by title before the New York meeting of the American Chemical Society, December 28, 1898.

² This Journal, 3, 103, 110, (1881).

This product was marked "A" and set aside for further examination.

The main crystalline mass or product "B", resulting from the action of sulphuric acid on thymol, was dissolved in hot water and filtered from a small quantity of a dark oily-looking liquid which floated on its surface and which appeared to be thymol. The filtrate was then neutralized with barium carbonate, filtered from the barium sulphate, and concentrated on the water-bath, till crystals began to show on the surface of the liquid. It was then set aside to crystallize.

A large crop of white flat-sided prisms was obtained. These were sucked as free from mother-liquid as possible, by the aid of a suction-pump and, after pressing between folds of filter-paper, were redissolved in a small quantity of hot water and the solution set aside to crystallize.

A barium salt "B" is thus obtained, which contains water of crystallization, a part of which is lost on exposure to the air, or over sulphuric acid, and the whole of it is driven off under partial decomposition of the salt, when the latter is heated to 100°.

One of the peculiarities of this salt, is the fact that it crystallizes from water in several crystalline forms, according as to whether the crystallization is allowed to take place gradually or rapidly.

By the slow evaporation of its aqueous solution, it is obtained in the shape of rhombic plates or prisms (Figs. 1 and 2). By a more rapid evaporation of the aqueous solution, it may be obtained in striated crystals, radiating from a common center (Fig. 3).

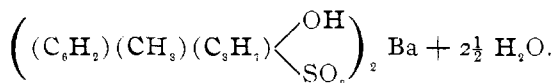
0.9324 gram substance, dried at 100°, lost 0.0724 gram water, equal to 2.55 molecules,—or in round numbers 2½ molecules of water of crystallization.

0.760 gram substance, dried at 100°, gave 0.2961 gram barium sulphate.

	Theory for	
	$\left((C_8H_8)(CH_2)(C_3H_7) \begin{matrix} \text{OH} \\ \text{SO}_3 \end{matrix} \right)_2 \text{Ba.}$	
Ba.....	23.02	Found. 22.90
2½ H ₂ O.....	7.03	7.84

Therefore the barium salt of what I will temporarily call

alphathymolsulphonic acid has the following empirical formula:



A comparison of my product with the barium salt of the alphathymolsulphonic acid, described by Engelhardt and Latschinoff,¹ shows that they are identical in all respects, save the water of crystallization. Engelhardt and Latschinoff claim two molecules of water of crystallization for their barium salt, while I find that mine crystallizes with two and one-half molecules of water of crystallization.

The barium salt of alphathymolsulphonic acid, above described, is very easily soluble in water and alcohol, from which, as already stated, it crystallizes in various forms, dependent upon the manner in which crystallization is brought about.

FREE ALPHATHYMOLSULPHONIC ACID.

In one of my previous papers² a method was described for obtaining this compound from its lead salt, by precipitating the lead with hydrogen sulphide. It may, however, also be prepared from its barium salt, by treating the latter with sufficient sulphuric acid to precipitate out all the barium present as barium sulphate. The latter is then collected upon a filter, washed, and the filtrate concentrated to the consistency of a sirup on the water-bath. On standing, the free thymolsulphonic acid crystallizes out, in the shape of rhombic plates or tables (Fig. 4). If, however, the sirup be agitated, or better still, if the bottom of the crystallizing dish be scratched with a glass rod, the sulphonic acid will be obtained in the shape of rhombic prisms grouped together fern-shaped and may at times be accompanied by some rhombic plates (Fig. 5). It is freely soluble in both hot and cold water and, as previously noted, was found to melt at 91°–92° C. Since in my previous papers no attempt was made to determine the true constitution of this interesting body, it was thought that a little more light upon the subject would not only be interesting but desirable. To gain this information, it was decided to submit the sulphonic acid to the action of oxidizing agents, with the view, if possible, of converting it into a

¹ *Ztschr. Chem.*, 1869, p. 44.

² *This Journal*, 3, 111 (1882).



FIG. 1.



FIG. 2.

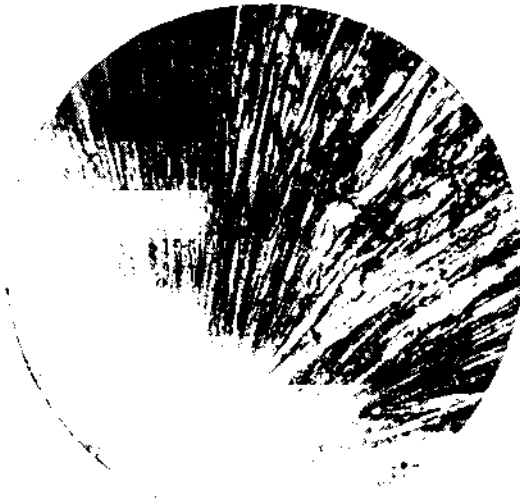


FIG. 3.



FIG. 4.



FIG. 5.

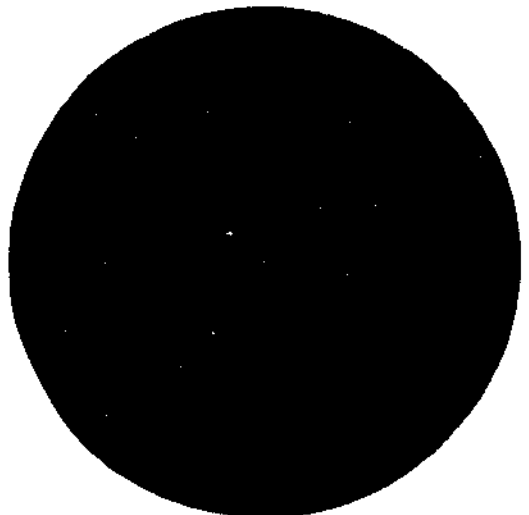
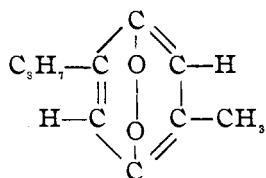


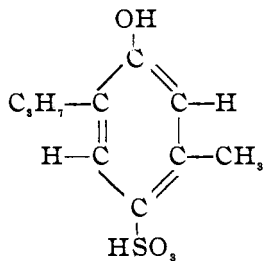
FIG. 6.

quinone, and from it determine the true constitution of the thymolsulphonic acid. For this purpose the following experiment was made :

Ten grams of the sodium salt of alphathymolsulphonic acid were dissolved in 100 cc. of water and to the solution was added a solution of thirty grams potassium bichromate, and ten grams of 66° sulphuric acid in 100 cc. of water. The mixture was now heated under a reflux condenser for about one-half hour and then submitted to steam distillation. A yellow oily liquid of penetrating and peculiar smell, passes over with the steam, and solidifies partly in the condenser and partly in the recipient, to a mass of yellow crystalline leaflets. These after recrystallization from alcohol and water, have the constant melting-point of 45.5°, and unite with hydroxylamine chloride to form a well-characterized oxime. From the above and its general characteristics, it was identified as thymoquinone of the following constitution :



Therefore as in the process of oxidation, the HSO_3 group and OH group are necessarily replaced by the two CO-groups, it follows that the constitution of my thymolsulphonic acid must be represented by the following formula :



That is, the HSO_3 group stands in the para position, in relation to the OH group.

It has also been shown by Ad. Claus,¹ that Engelhardt and Latschinoff's alpthymolsulphonic acid, is a parasulphonic acid, and as my acid is identical with their product, it follows that this is an additional proof of the correctness of the constitutional formula above set forth.

Engelhardt and Latschinoff² mention two other isomeric thymolsulphonic acids, which they obtained simultaneously with the para acid, and which they designate as the β - and γ -acid.

These are separated from the para acid by the difference in solubility of their potassium salts, the potassium salt of the para acid being much more freely soluble than the potassium salt of the β -acid (according to Claus, the β -acid is the orthosulphonic acid and the γ -acid, a mixture of para and disulphonic acids).

It therefore seemed possible that by my mode of operating, isomeric acids might likewise be formed and to settle this question the following experiment was made :

The mother-liquor separated from the barium salt of thymolparasulphonic acid, was diluted with water, heated to boiling and treated with sufficient potassium carbonate, to precipitate all the barium present, as barium carbonate. The latter was collected upon the filter, washed with hot water and the filtrate concentrated to a small volume by evaporation; no crystals of a difficultly soluble potassium salt separated on cooling, hence Engelhardt and Latschinoff's β -sulphonic acid or thymolorthosulphonic acid was absent. As a further evidence of the absence of the ortho acid, the above solution was evaporated to dryness, and the dry residue dissolved in ninety per cent. alcohol, in which it is very soluble. On cooling no separation of a difficultly soluble potassium salt occurred and it is only after evaporating the alcoholic solution to the consistency of a sirup and allowing the latter to cool, that I was finally able to obtain the potassium salt in a crystalline form. The product thus obtained crystallizes from alcohol, in rhombic crystals which are freely soluble both in alcohol and water. From water it crystallizes in flat-sided needles. A comparison of this salt, with the potassium salt of thymolparasulphonic acid described by Engelhardt and Latschinoff, shows that they are identical.

¹ *J. prakt. Chem.*, 43, 334-355.

² *Loc. cit.*

The oily product "A" referred to in the early part of this paper, as being formed in small quantity by the action of sulphuric acid on thymol, at 100°, crystallizes on cooling to a white crystalline mass which, when viewed under the microscope, is seen to be composed of a multitude of little white needles (Fig. 6). The product was dissolved in cold water, heated to boiling, and neutralized with barium carbonate. The barium sulphate formed was collected upon a filter, washed with hot water, and the filtrate concentrated to a small volume on the water-bath.

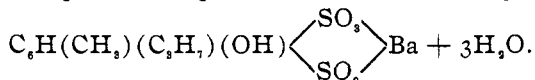
After several weeks' standing a barium salt was obtained which crystallized in long white needles, some of which were two or three centimeters long. The yield of this product was, however, very small, hardly enough for analysis being obtainable. It is exceedingly soluble in water and for this reason is difficult to obtain in a crystalline form. It crystallizes with water of crystallization.

0.3399 gram salt, dried at 100°, lost 11.29 per cent. water.

0.3012 gram salt, dried at 100°, gave 0.1472 gram barium sulphate.

	Theory for	
	$\text{C}_6\text{H}(\text{CH}_3)(\text{C}_3\text{H}_7)\text{OH} \left\langle \begin{array}{l} \text{SO}_3 \\ \text{SO}_3 \end{array} \right\rangle \text{Ba} + 3\text{H}_2\text{O}.$	
H ₂ O	13.53	Found,
Ba.....	30.78	11.29
		28.71

From the above it is evident that the barium salt analyzed was not pure, but as the figures obtained agree much better with the theory for a disulphonid acid than anything else coupled with the great solubility of the barium salt, I am inclined to believe that what I had in hand, was a barium salt of thymoldisulphonic acid, which is probably represented by the following formula :



Owing to the small quantity of material at my disposal, a more thorough examination of this salt was impossible.

To recapitulate, it will therefore be seen that the only two products formed by the action of 66° sulphuric acid on thymol, at the temperature of boiling water, are thymolparasulphonic acid and thymoldisulphonic acid, of which the former constitutes by far the greater portion, while the latter product is only obtained in very small quantity.