

DETERMINATION OF THIOBENZOIC ACID WITH CHLORAMINE-T AND DICHLORAMINE-T

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THIOBENZOIC acid is widely used as a catalyst for the synthesis of polymers of vinyl imidazolines and vinyl tetrahydropyrimidines. In view of the ability of chloramine-T to rupture C-S, N-S, S-S and P-S bonds in a variety of sulphur compounds¹⁻¹² oxidising the entire sulphur to sulphuric acid, and dichloramine-T being an oxidimetric reagent in non-aqueous¹³ and partially non-aqueous¹⁴ media, it was of interest to study the reactions of thiobenzoic acid with chloramine-T (CT) and dichloramine-T (DCT). The results of such studies are presented in this communication.

Reagents.—Fluka AG "Guaranteed Reagent Fro Analysis" Thiobenzoic acid was employed for the present work. Standard solutions of thiobenzoic acid were prepared in glacial acetic acid. Stock solutions of chloramine-T and dichloramine-T were prepared, standardized and preserved, in conformity with the recommendations of Bishop and Jennings¹⁵ and the present authors¹³⁻¹⁴ respectively.

Procedure.—(a) With chloramine-T in alkaline medium: Measured aliquots of the chloramine-T solutions were taken in 500 ml. glass-stoppered conical flasks and 30 ml. of 5N sodium hydroxide were added to each. Known volumes of the standard thiobenzoic acid solutions were now introduced with shaking. The mixtures were heated to 60° C. and kept at that temperature for about half an hour, when the solutions became clear. The solutions were cooled to room temperature and excess of 5N sulphuric acid and 15 ml. 10% aqueous potassium iodide were added. The liberated iodine was estimated by titrating it with standard thiosulphate solution. From the amount of chloramine-T consumed, the ratio of equivalents of oxidant consumed per mole of thiobenzoic acid was calculated. Typical results are given in Table I.

(b) With dichloramine-T in non-aqueous medium: Measured aliquots of the dichloramine-T were taken in a glass-stoppered conical flask and added 30 ml. of glacial acetic acid, 5-10 ml. water and a sample aliquot of the thiobenzoic

TABLE I
Oxidation of Thiobenzoic Acid by Chloramin-T

Exp. No.	Millimoles of thiobenzoic acid taken	Milliequivalents of chloramine-T consumed	No. of equivalents of oxidant consumed per mole of thiobenzoic acid
1	0.2016	1.615	8.009
2	0.2521	2.018	8.004
3	0.2521	2.027	8.041
4	0.3529	2.822	7.997
5	0.4033	3.223	7.993

acid solution. With the stopper in place allowed the flask to remain 30 to 40 minutes at room temperature (28° C). Diluted to 200 ml. with water, added 10% aqueous potassium iodide solution and titrated the liberated iodine with standard thiosulphate solution to the starch end point. From the amount of dichloramine-T consumed, the ratio of equivalents of oxidant consumed per mole of thiobenzoic acid was calculated. Typical results are given in Table II.

TABLE II
*Oxidation of Thiobenzoic Acid by
Dichloramine-T*

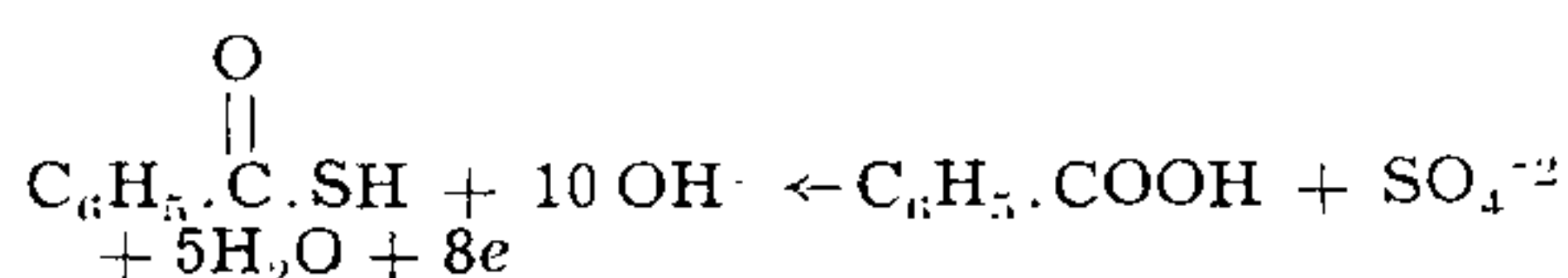
Exp. No.	Millimoles of thiobenzoic acid taken	Milliequivalents of dichloramine-T consumed	No. of equivalents of oxidant consumed per mole of thiobenzoic acid
1	0.2614	2.086	7.982
2	0.2614	2.076	7.943
3	0.3025	2.439	8.063
4	0.3529	2.821	7.995
5	0.4033	3.228	8.005

Blanks were run concurrently for both; no blank corrections were necessary.

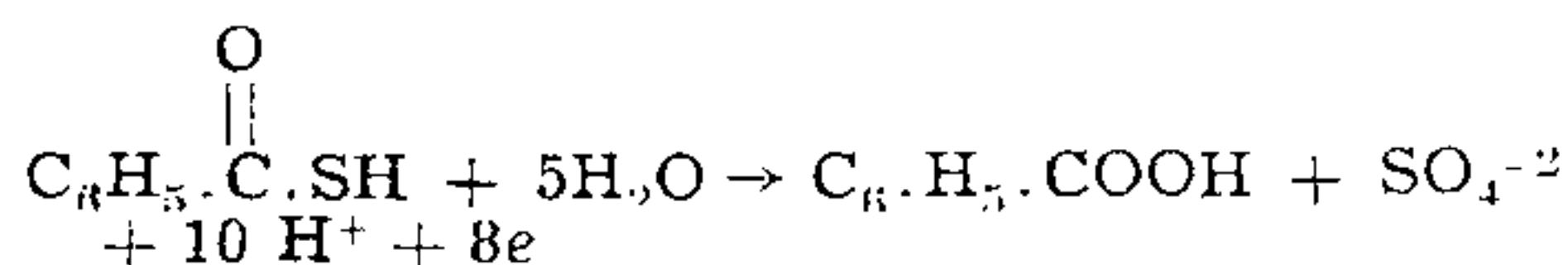
Results and Remarks.—It may be seen from the Tables I and II that eight equivalents of oxidant are consumed per mole of thiobenzoic acid.

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This is in agreement with the following oxidation schemes.



(in alkaline medium with CT)



(in acid medium with DCT).

The large number of equivalents consumed per mole of the substance indicates that the chloramine-T and dichloramine-T oxidation methods should be very accurate analytical procedures for the estimation of thiobenzoic acid in aqueous and non-aqueous media, respectively, in which traces of water accelerate the oxidation.

Independent experiments carried out by the present authors have shown that benzoic acid is not further oxidised by chloramine-T under the experimental conditions.

The oxidation of thiobenzoic acid by chloramine-T was studied under various conditions. The oxidation was found to be incomplete in acid medium at room temperature (28° C.). The data obtained at elevated temperatures were inaccurate. Oxidation in alkaline medium was found to be incomplete at room temperature; a

turbidity due to partial separation of elemental sulphur was visible in this case. The turbidity disappeared on warming to 60° C. Finely divided sulphur is known to react quantitatively with alkali forming a mixture of sulphide, sulphite and thiosulphate,¹⁶ all of these sulphur oxianions are further oxidised by chloramine-T to the sulphate ion.⁸

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