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## Reaction of Dithizone with Alkylmercuric and Trimethylmercurioxonium Salts

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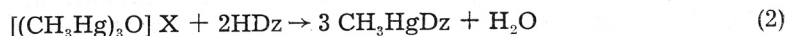
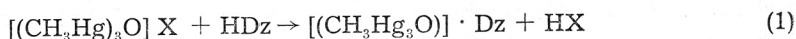
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The action of dithizone on trimethylmercurioxonium salts has been investigated, and the corresponding dithizonate complex has been isolated. The reaction of dithizone with alkylmercuric halides as well as their salts of oxyacids has been investigated too. Mercuric bis-dithizonate could not be found among the products of these reactions, which disprove the existing data. The reactions were studied spectrophotometrically.

In the course of investigation of trimethylmercurioxonium salts<sup>1,2</sup> we have tried to find such characteristic reagents by which we should be able to distinguish at least qualitatively, trimethylmercurioxonium from methylmercuric (or any alkylmercuric) ion, in a given mixture. Since dithizone is a well known analytical reagent, not only for alkylmercuric but for phenylmercuric ion as well<sup>3,4</sup>, we have tried to apply the same reagent to trimethylmercurioxonium ion.

Dithizone (as a weak acid, in further text HDz) gives with alkylmercuric salts corresponding dithizonates RHgDz with absorption maximum in ethanolic solution at 480 m $\mu$ <sup>5</sup>. We found that the reaction of trimethylmercurioxonium salts with dithizone is analogous, trimethylmercurioxonium dithizonate being the product, giving an absorption maximum at 510 m $\mu$  in ethanolic solution.

As expected, trimethylmercurioxonium dithizonate reacted with excess dithizone, destroying oxonium structure, with formation of more stable methylmercuric dithizonate



Since trimethylmercurioxonium salts are very sensitive to acids (strong acid is liberated during the reaction) the first reaction was always carried out in a buffered solution.

Dilute solutions of trimethylmercurioxonium dithizonate ( $10^{-3}$  M or lower) in ethanol or chloroform, are not stable, due to dissociation of trimethylmercurioxonium to more stable methylmercuric dithizonate. The dissociation was almost complete at concentrations of about  $10^{-5}$  M where we found the absorption maximum at 480 m $\mu$  instead of 510 m $\mu$ . If an excess of trimethylmercurioxonium ion is present, the dissociation is hindered. Thus, the absorption maximum at 480 m $\mu$  of a trimethylmercurioxonium dithizonate solution of  $5.5 \cdot 10^{-5}$  M concentration in ethanol is shifted to the value of 510 m $\mu$ , if the

solution of the same concentration is made in  $10^{-2} M$  ethanolic solution of trimethylmercurioxonium perchlorate.

The instability of diluted solution of trimethylmercurioxonium dithizonate in ethanol (or in other solvents) eliminates every possibility of the application of dithizone for the quantitative determination of trimethylmercurioxonium salts.

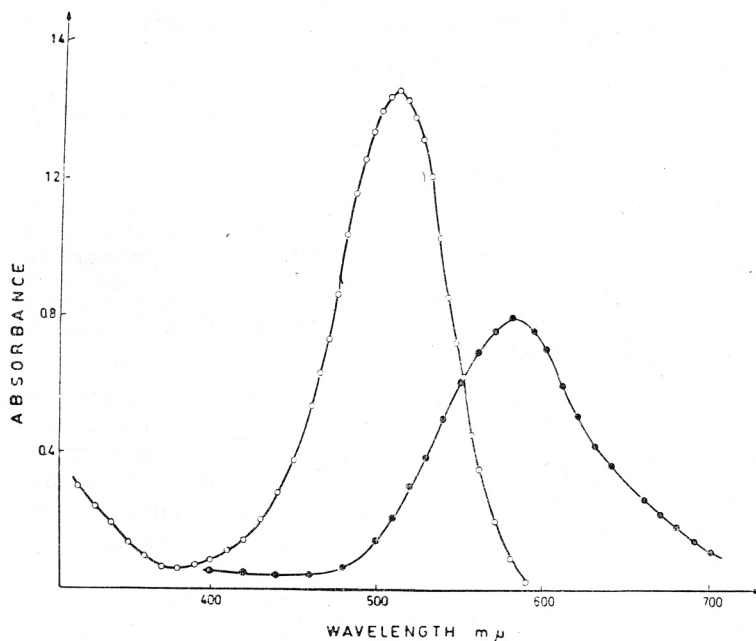


Fig. 1. Absorption curves of trimethylmercurioxonium dithizonate in ethanol ( $4 \cdot 10^{-5} M$  in  $10^{-2} M$  solution of trimethylmercurioxonium perchlorate) and trimethylmercurioxonium diphenyl carbazonate in ethanol ( $8 \cdot 10^{-5} M$  in  $10^{-2} M$  solution of trimethylmercurioxonium perchlorate).

The reaction of diphenylcarbazonate with trimethylmercurioxonium ion, as well as with methylmercuric ion, is similar to that of dithizone. Diphenylcarbazonate gives with methylmercuric salts (in chloroform) a solution with absorption maximum at  $570 m\mu$ , while for trimethylmercurioxonium salts, under the same conditions, the solution shows an absorption maximum at  $580 m\mu$ . In Fig. 1 absorption curves of trimethylmercurioxonium dithizonate and diphenylcarbazonate, respectively, are given.

It is to be added here that eventually we have found a specific (precipitating) reagent for trimethylmercurioxonium salts. Saturated aqueous solution of thiourea gives a precipitate of methylmercuric sulphide with concentrated aqueous solution of trimethylmercurioxonium salts. Methylmercuric and other alkylmercuric salts do not react in this manner. On the other hand, they are precipitated from the concentrated ethanolic solution with rubeanic acid in the form of methylmercuric sulphide. Trimethylmercurioxonium salts do not interfere.

Special attention was paid to the study of characteristic reactions of alkylmercuric dithizonates with respect to their application in quantitative analysis of alkylmercuric salts. In the literature there are different statements on the

behaviour of alkylmercuric dithizonates in excess of dithizone and in the presence of a strong acid, which have to be examined.

J. L. A. Webb and coworkers<sup>5</sup> carried out numerous experiments on reaction of dithizone with various types of alkyl and arylmercuric compounds. Among them, they paid special attention to the investigation of formation and properties of ethylmercuric dithizonate. They pointed out that in the reaction of an alkylmercuric halide (ethylmercuric chloride), dithizone acts as an acid, *viz*:



Webb and coworkers reported that the reaction occurred in unbuffered solution, indicating the importance of liberated acid. One would not expect the carbon-mercury bond to be cleaved, because this bond is rather inert. We tried to repeat the experiments described by Webb and coworkers in order to examine this reaction in more details.

The cleavage of carbon-mercury bond could be explained by the influence of these two factors:

- a) reactions of strong acid liberated (hydrochloric acid)
- b) influence of the sulphhydryl group of enolic form of dithizone.

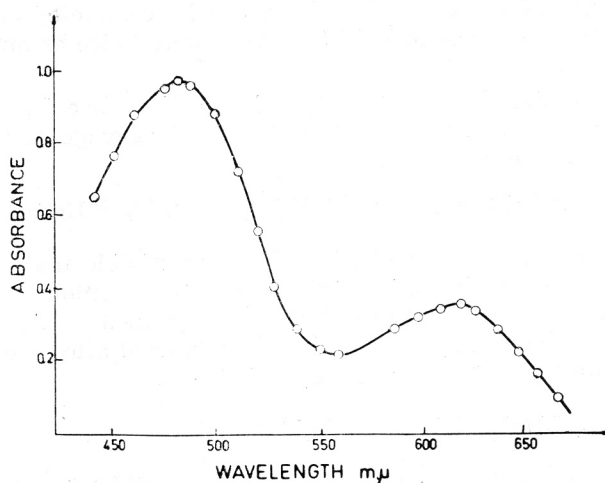


Fig. 2. Absorption curve of a chloroform solution of ethylmercuric chloride with dithizone in a molar ratio of 1 : 2.

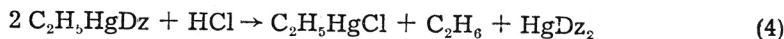
It is well known that carbon-mercury bond in alkylmercuric salts is rather inert. The bond is untouched even under the action of diluted halogen acids<sup>6</sup>, sulphide or sulphhydryl ion<sup>7</sup>. In the reaction of ethylmercuric chloride, in chloroform, with twice as much as stoichiometric quantity of dithizone, a product with absorption curve shown in Fig. 2 was obtained. The product was a mixture of dithizone itself (distinct maximum at 620 mμ where mercuric dithizonates do not absorb) and ethylmercuric dithizonate (with absorption maximum at 480 mμ). This mixture was then separated by fractional crystallization from chloroform, and components were identified chemically and spectrophotometrically as dithizone and ethylmercuric dithizonate.

In an analogous experiment ethylmercuric chloride, in chloroform, was mixed with dithizone in the molar ratio 1:2. The solution was shaken several times with water, in order to remove hydrochloric acid formed. The solution was then treated with ethylmercuric chloride solution, until the dark brown colour changed to orange. During the addition of ethylmercuric chloride, the solution was shaken with an aqueous ammonium acetate (buffer). The colour change was very sharp. The quantity of ethylmercuric chloride added in that »titration« showed that nearly one mole of stoichiometric excess of dithizone was present in the solution. The absorption curve of the solution obtained had the maximum at 477  $\mu$  *i. e.* the same as the solution of pure ethylmercuric dithizonate.

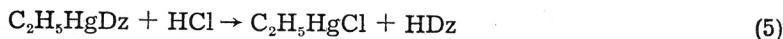
It is important to mention here, that mercuric bis-dithizonate (which, according to Webb and coworkers<sup>5</sup> should be formed by the reaction of ethylmercuric chloride with dithizone in excess), does not react with ethylmercuric chloride. The mercuric bis-dithizonate in chloroform retains its absorption maximum (490  $\mu$ ) even after addition of considerable amount of ethylmercuric chloride.

Our experiments described above, showed that ethylmercuric dithizonate does not react with dithizone. The reaction between ethylmercuric chloride and dithizone in unbuffered acid medium can be completed only in the presence of considerable excess of DzH (approximately twice as much as stoichiometrical ratio).

The action of strong halogen acids with ethylmercuric dithizonate, according to the same authors<sup>5</sup>, is accompanied by the cleavage of carbon-mercury bond, according to the equation:



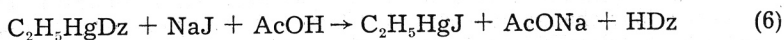
According to our experiments, it is hardly probable that such a reaction proceeds in described manner. For this reason this reaction was carefully re-examined. The result was different from the described one. The considerable part of ethylmercuric dithizonate remained unchanged after the action of acid, while a small quantity of dithizone separated:



Hydrochloric acid, therefore, does not cleave carbon mercury bond, but displaces dithizone as a weaker acid, forming weakly ionized ethylmercuric chloride. The equilibrium of this reaction depends on hydrochloric acid concentration. It was observed, that the reaction does not proceed until  $pH \sim 3$  (ethanolic solution of hydrochloric acid measured with »Merck« universal indicator paper), when the separation of dithizone began. At  $pH \sim 2.5$  the separation of dithizone was completed, which was proved by spectrophotometric measurement. The solution had the absorption curve, which corresponded to that of dithizone. After partial neutralization of the solution ( $pH$  value increased to  $\sim 3.5$ ) the equilibrium of the reaction was moved completely to the left and showed all characteristics of an ethylmercuric dithizonate solution. The action of hydroiodic acid was similar to that of hydrochloric acid, except that its action (the separation of dithizone) was observed at  $pH$  values from 6 to 6.5. We can therefore conclude that the reaction (5) depends primarily on anion qualities *i. e.* on stability

constants of ethylmercuric halogenide formed, and that hydrogen ion concentration is of less importance.

The validity of this conclusion has been proved by the experiments with oxyacids, *e. g.* sulphuric, perchloric *etc.* No reaction between ethylmercuric dithizonate and oxyacid was observed, even at very low pH values, when the content of an oxyacid in solution reached several percent. However, reaction (5) could be positive even with small quantity of weak oxyacid (for instance few drops of 0.5 percent acetic acid in ethanolic solution) if sodium iodide is present:



By using alkylmercuric sulphate (as a salt of an oxyacid), the isolation of alkylmercuric dithizonate was possible. In this way we succeeded to prepare ethylmercuric dithizonate by reaction of stoichiometric amount of ethylmercury sulphate and dithizone. This preparation is impossible, if starting with ethylmercuric halides.

Methylmercuric dithizonate was also prepared. Its chemical reactions were analogous to those described for ethyl derivative, as well as its absorption curve, given in Fig. 3.

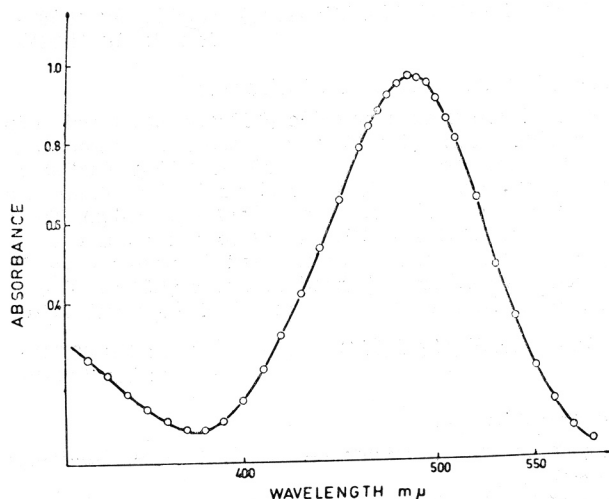


Fig. 3. Absorption curve of an ethanolic solution of methylmercuric dithizonate ( $4.10^{-5}$  M).

#### EXPERIMENTAL

##### *The preparation of trimethylmercurioxonium dithizonate*

Trimethylmercurioxonium perchlorate (0.80 g., 0.00105 moles) was dissolved in methanol (2 ml.). Chloroform (20 ml.) and an aqueous solution of ammonium acetate (0.5 in 15 ml.) was added to the solution. This mixture was shaken for half an hour with the solution of dithizone in chloroform (0.27 g., 0.00105 moles in 25 ml.), which was added in portions of 5 ml. every five minutes. The lower, dark red coloured chloroform layer was separated, washed with water ( $4 \times 20$  ml.) and dried over anhydrous sodium sulphate (15 g.). The solution was evaporated at  $50^\circ\text{C}$  and 17 mm Hg

to a volume of about 5 ml. Ethanol was added (10 ml.) and the solution cooled, until dark violet crystals were precipitated, which were filtered off and washed with ether ( $2 \times 5$  ml.). Yield 0.77 g. The compound was recrystallized from chloroform-ethanol mixture. Melting point  $169^{\circ}\text{C}$  with decomposition.

Anal.  $[(\text{CH}_3\text{Hg})_3\text{O}]\text{C}_{13}\text{H}_{11}\text{N}_4\text{S}$  (917.8) calc'd.: Hg 65.56%  
found: Hg 65.71%

#### *Titration of trimethylmercurioxonium dithizonate solution*

Trimethylmercurioxonium dithizonate solution in chloroform (5 ml.  $5.23 \times 10^{-3} M$ ) was titrated with dithizone solution in chloroform ( $1.84 \times 10^{-3} M$ ) to the moment when a sharp colour change of dark red (trimethylmercurioxonium dithizonate) to orange (methylmercuric dithizonate) was observed. The volume of 29.2 ml. of dithizone solution was used.

#### *The preparation of ethylmercuric dithizonate without buffer*

A solution of ethylmercuric sulphate (0.65 g., 0.00117 moles) in methanol (3 ml.) was diluted with chloroform (40 ml.) and mixed with a dithizone solution (0.60 g., 0.00234 moles) in chloroform (30 ml.). The red coloured solution was shaken for 10 minutes, washed with water ( $4 \times 20$  ml.) dried over anhydrous sodium sulphate (15 g.), and evaporated *in vacuo* ( $50^{\circ}\text{C}$  and 17 mm Hg) to a volume of about 5 ml. Ethanol was then added (10 ml.) and the solution cooled until irregular red crystals of ethylmercuric dithizonate were separated, filtered off, and washed with ether ( $2 \times 5$  ml.). Yield 0.785 g. Melting point  $157.5^{\circ}\text{C}$ .

Anal.  $\text{C}_2\text{H}_5\text{HgC}_{13}\text{H}_{11}\text{N}_4\text{S}$  (482.6) calc'd.: Hg 41.58%  
found: Hg 41.32%

#### *The preparation of methylmercuric dithizonate*

A solution of methylmercuric bromide (0.88 g., 0.00298 moles) in methanol (5 ml.) was diluted with chloroform (20 ml.), mixed with an ammonium acetate solution (0.7 g. in 15 ml. of water) and dithizone solution (0.75 g., 0.00298 moles in 15 ml. of chloroform). The mixture was shaken for about half an hour, washed with water ( $4 \times 20$  ml.) and dried over anhydrous sodium sulphate (15 g.). The solution was then evaporated *in vacuo* at  $50^{\circ}\text{C}$  and 17 mm Hg to the volume of about 5 ml., when ethanol (10 ml.) was added. After cooling, red irregular crystals were separated, filtered off, washed with ether and dried *in vacuo* (1.35 g.). The compound was recrystallized from chloroform-ethanol mixture. Melting point  $146^{\circ}\text{C}$ .

Anal.  $\text{CH}_3\text{HgC}_{13}\text{H}_{11}\text{N}_4\text{S}$  (470.6) calc'd.: Hg 42.73%  
found: Hg 42.58%

#### *Spectrophotometric Measurements*

For all the experiments Hilger — Watts Uvispec spectrophotometer Model H 700.307 was used.

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#### REFERENCES

1. D. Grdenić and F. Zado, *Croat. Chem. Acta* **29** (1957) 425.
2. D. Grdenić and F. Zado, *J. Chem. Soc.* **1962**, 321.
3. V. L. Miller, D. Polley, and C. J. Gould, *Anal. Chem.* **23** (1950) 1282.
4. V. L. Miller and D. Polley, *Anal. Chem.* **26** (1954) 1333.
5. J. L. A. Webb and coworkers, *J. Am. Chem. Soc.* **74** (1950) 91.
6. K. H. Slotta und K. R. Jacobi, *J. Prakt. Chem.* **120** (1929) 249.
7. D. Grdenić and B. Markušić, *J. Chem. Soc.* **1958**, 2434.

**IZVOD****Reakcija ditizona sa alkilmerkuri i trimetilmerkurioksonijevim solima***F. Zado*

Ispitano je djelovanje ditizona na trimetilmerkurioksonijeve soli te je izoliran odgovarajući ditizonat. Istraživano je također djelovanje ditizona na alkilmerkuri halogenide i njihove soli oksikiselina. Kao produkt ovih reakcija merkuri bis ditionat nije mogao biti dokazan, kako je do sada bilo opisano. Reakcije su ispitivane spektrofotometrijski.

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ZAGREB

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