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I.—THIOPHTHALIC ACIDS. PART I.[1]

By Gopâl Chandra Chakravarti.

Various attempts have been made since 1874 to synthesise two important acids, namely mono- and dithiophthalic acids. But up till now these endeavours have proved fruitless. In 1874 Schreder (*Ber.*, 1874, **7**, 704) treated phenyl phthalate in alcoholic solution with potassium hydrosulphide and appears to have obtained a very impure potassium thiophthalate from which hydrochloric acid set free the body $C_8H_4O_2S$. This body corresponds with thiophthalic anhydride and not with the acid. He represented the reaction by the following equations :—

$$C_6H_4(CO_2{\cdot}C_6H_5)_2 + 2KSH = C_6H_4(CO{\cdot}SK)_2 + 2C_6H_5{\cdot}OH.$$

$$C_6H_4(CO{\cdot}SK)_2 + 2HCl = C_6H_4\begin{<}\begin{matrix}CO\\CO\end{matrix}\end{>}S + H_2S + 2KCl.$$

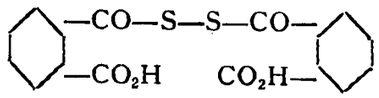
(I)

In 1884 Graebe and Zschokke (*Ber.*, 1884, **17**, 1175) found that thiophthalic anhydride and not the acid is obtained by acidification of the solution obtained by slowly adding phthalyl chloride to a cold concentrated solution of sodium hydrogen sulphide. Later Reissert and Holle (*Ber.*, 1911, **44**, 3027) prepared a number of derivatives of both mono- and dithiophthalic acids starting from thiophthalic anhydride, but concluded like the previous investigators that these acids were somewhat stable in the form of their alkali salts in aqueous solutions, whereas the free acids were extremely unstable and therefore could not be obtained as such, the acids decomposing immediately into thiophthalic anhydride, m. p. 114°, and hydrogen sulphide.

Recently the author (Chakravarti and Saha, *J. Indian Chem. Soc.*, 1927, **4**, 141) made an attempt to condense phthalic anhydride with aromatic mercaptans in order to obtain dyes analogous to the phthaleins, but found that the great reactivity of the mercaptanic hydrogen atoms led to the formation of thiophthalic esters instead of the thiophthaleins. In that communication the authors expressed their intention of utilising the thiophthalates for the syntheses of mono- and dithiophthalic acids. By carrying out the hydrolysis of ditolyl dithiophthalate with alcoholic potassium hydrosulphide under various conditions, an acid containing sulphur and melting at 242° with decomposition was obtained. The acid however did not respond to the ordinary tests for a 'thiol' group and the determination of its equivalent showed that it had a molecular weight almost double that

[1] Reprinted from the *Journal of the Indian Chemical Society*, 1928, **5**, 405.

required by monothiophthalic acid and was therefore dithiodibenzoyl-*oo'*-dicarboxylic acid (II).



(II)

The formation of this acid at once suggested that at an intermediate stage monothiophthalic acid must have been produced, and the latter might be obtained if the reaction could be properly moderated. But at a lower temperature the hydrolysis of the thio-ester would not take place. Hence a study of the interaction of potassium hydrosulphide and phthalyl chloride in alcoholic solution seemed desirable. It was found that the reaction proceeds very briskly even in the cold and from the products a number of compounds together with monothiophthalic acid have been isolated. A description of these products and their method of isolation is given in the experimental portion. From a study of the properties of monothiophthalic acid, the author generally agrees with the views expressed by previous investigators about the extreme instability of the acid, but the hypothesis that it breaks down immediately on formation into thiophthalic anhydride should once for all be discarded. Because under ordinary conditions the anhydride was never obtained by the decomposition of the acid; the product invariably obtained was the corresponding disulphide, dithiodibenzoyldicarboxylic acid, evidently formed by the oxidation of the mercaptanic hydrogen atom. In fact the acid is so very reactive towards oxygen that it is oxidised by the atmosphere even during processes of purification and crystallisation; so that for a long time the disulphide was looked upon as the initial product of the reaction.

In the operations a sample of crystallised potassium hydrosulphide supplied by Kahlbaum was used. As this contains water of crystallisation it is very difficult to indicate the exact mechanism of the reaction, which may have taken either of the courses :—

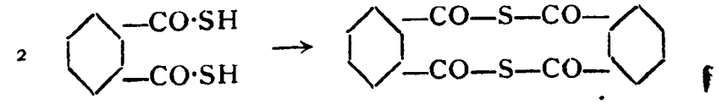
$$C_6H_4(COCl)_2 + 2KSH = C_6H_4(CO\cdot SH)_2 + 2KCl.$$

$$C_6H_4(CO\cdot SH)_2 + H_2O = C_6H_4\begin{cases} CO\cdot SH \\ CO_2H \end{cases} + H_2S \qquad (1)$$

or

$$C_6H_4(COCl)_2 + KSH + H_2O + KSH = C_6H_4\begin{cases} CO\cdot SH \\ CO_2H \end{cases} + 2KCl + H_2S \qquad (2)$$

Of the two alternatives, reaction (1) appears to be the more likely, because although the dithio-acid has not been isolated in the pure state its existence has been confirmed from various facts. The extract obtained by aqueous carbonated alkalis from the ethereal solution of the reaction product on acidification gives a precipitate of the monothio-acid or more generally its disulphide mixed with an acidic oil with very strong characteristic disagreeable odour. This oily acid gradually diminishes in quantity during purification and more and more of the solid acid is produced. This change therefore represents the second phase of reaction (1) Moreover, when the ethereal solution of the mixture of acids, or their aqueous alkaline solution is kept exposed to the air for some time a yellow precipitate insoluble in alkalis begins to appear which can only be formed by the elimination of hydrogen sulphide from dithiophthalic acid, or of alkaline sulphides from its alkaline solutions :



In fact when such an alkaline solution is acidified after removal of the yellow precipitate, hydrogen sulphide is evolved plentifully and simultaneously thiophthalic anhydride is formed in considerable quantity by the elimination of one molecule of hydrogen sulphide from a molecule of the acid. Thus dithiophthalic acid undergoes a threefold decomposition into monothiophthalic acid, thiophthalic anhydride and diphthalyl disulphide. The crude acid could not be purified from admixture with solvents and the monothio-acid on account of its extreme instability, and is under further investigation.

EXPERIMENTAL.

Potassium hydrosulphide (12 gms.) is mixed with 125 c.c. of absolute alcohol and saturated with sulphuretted hydrogen in the cold and then gradually added to a cold solution of phthalyl chloride (15 gms.) in 75 c.c. of alcohol. A vigorous reaction at once begins. The reaction-bottle is well corked, cooled by a freezing mixture to -5° and allowed to stand for half an hour with occasional shaking. Then the vessel is removed to a shaking machine and the reaction is allowed to proceed there for about three hours at a temperature not exceeding 10°, and then the mixture allowed to stand overnight. The contents of the bottle are next poured on to about a litre of ice-water and the aqueous mixture extracted with ether. The ethereal extract is washed thoroughly with cold water and then neutralised with a slight excess of a cold solution of sodium carbonate. A yellow precipitate (A) which is neither soluble in alkali nor in ether separates out at this

stage and is removed. The ethereal extract (B) is kept for further treatment.

A part of the alkaline extract is neutralised with cold dilute hydrochloric acid and the precipitate extracted with ether. This ethereal solution is dried over anhydrous magnesium sulphate and on slow evaporation deposits needle-shaped crystals, which are found to be difficultly soluble in ether. The product is therefore crystallised from a large quantity of absolute alcohol and obtained in the form of very light cream-coloured minute crystals, melting about 242° with decomposition. These are found to correspond to dithiodibenzoyl-*oo'*-dicarboxylic acid (Found: C, 52·91; H, 2·84; S, 17·98. $C_{16}H_{10}O_6S_2$ requires C, 53·04; H, 2·76; S, 17·9 per cent.). The *potassium salt* is prepared by adding the calculated quantity of alcoholic caustic potash to an absolute alcoholic solution of the acid and evaporating part of the alcohol in a vacuum (Found: K, 18·01. $C_{16}H_8O_6S_2K_2$ requires K, 17·8 per cent.). The *lead salt* is obtained as a white crystalline precipitate by adding lead acetate solution to a solution of the potassium salt in water. The precipitate is washed with water, alcohol and ether (Found: Pb, 36·15. $C_{16}H_8O_6S_2Pb$ requires Pb, 36·5 per cent.). The remaining portion of the alkaline extract was converted into the lead salt by means of lead acetate solution and the lead salt washed with water and alcohol and thoroughly dried. The powdered lead compound is suspended in anhydrous ether and decomposed by passing sulphuretted hydrogen. The precipitate of lead sulphide is filtered off and the ethereal solution on concentration deposits almost colourless needle-shaped crystals of monothiophthalic acid which after recrystallisation from ether melts with decomposition at about 198° (Found: C, 52·22; H, 3·8; S, 17·24. $C_8H_6O_3S$ requires C, 52·74; H, 3·28; S, 17·56 per cent.). Monothiophthalic acid is readily soluble in ether and alcohol. Its conversion into the less soluble disulphide is so rapid in presence of air that even during the evaporation of its ethereal solution it becomes oxidised so that in the course of several preparations the disulphide-dicarboxylic acid was the only compound obtained in the final stage. The ethereal mother-liquor, after removal of the monothio-acid, leaves an oil with strongly acid character and characteristic disagreeable odour. From preliminary investigation this oil-acid is supposed to be dithiophthalic acid. Further investigation is in progress.

The *sodium salt* of monothiophthalic acid is obtained by adding the calculated quantity of aqueous sodium carbonate solution to an alcoholic solution of the acid. The filtered solution is concentrated to a small bulk, treated with absolute alcohol and again filtered. On keeping in contact with a small quantity of ether, the solution deposits colourless crystals of the sodium salt (Found: Na, 20·10. $C_8H_4O_3SNa_2$ requires Na, 20·3 per cent.). The *lead salt* is obtained by adding an alcoholic lead acetate solution to an alcoholic solution of the acid (Found: Pb, 53·21. $C_8H_4O_3SPb$ requires Pb, 53·48 per cent.).

The yellow precipitate (A) is washed with water, dried and repeatedly extracted with a large volume of alcohol. The alcohol removes a quantity of sulphur only. The deep yellow residue is dissolved in the minimum quantity of hot pyridine, which deposits on cooling a crop of very light, needle-shaped, egg-yellow crystals which do not decompose on heating to 320°. The compound is insoluble in ether, alcohol, benzene and alkalis, and is supposed to be diphthalyl disulphide (Found: S, 19·26. $C_{16}H_8O_4S_2$ requires S, 19·51 per cent.).

The ethereal solution (B) is dehydrated with anhydrous magnesium sulphate and then slowly evaporated. Colourless needle-shaped crystals, m.p. 114°, are obtained. They are identical with thiophthalic anhydride (Found: S, 19·42. $C_8H_4O_2S$ requires S, 19·51 per cent.). The ethereal mother-liquor, on complete evaporation, leaves an oil which is purified from admixed solid by distillation in steam. The distillate is extracted with ether, dehydrated by anhydrous magnesium sulphate, filtered and the ether completely removed first on the water-bath and finally in a vacuum over sulphuric acid. The constitution of the oil has not been determined.

Hydrolysis of Ditolyl dithiophthalate: Formation of Dithiodibenzoyl-oo'-dicarboxylic Acid.—Ditolyl dithiophthalate (10 gms.) and potassium hydrosulphide (7 gms.) are suspended in 75 c.c. of absolute alcohol and saturated with sulphuretted hydrogen. The mixture is heated in a sealed tube for 8–9 hours at 120°. The red solution is partially evaporated, treated with water and the aqueous solution decanted from the insoluble oil, cooled by ice and treated with dilute hydrochloric acid. The precipitated mass is next treated with sodium carbonate solution and the solution washed with ether, filtered and reprecipitated with cold dilute hydrochloric acid. The solid is washed with water and crystallised from absolute alcohol. Cream-coloured needle-shaped crystals, m.p. 242° (decomp.) identical with those of dithiodibenzoyl-*oo'*-dicarboxylic acid are obtained.

I desire to thank Sir P. C. Rây for his very kind interest and also Mr. R. K. Bhattacharyya for rendering valuable help in the analytical work.

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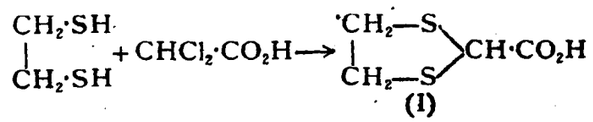
II.—ORGANIC CYCLIC POLYSULPHIDES: CONDENSATION OF ETHYLENE MERCAPTAN WITH DI- AND TRICHLORACETIC ACIDS.[1]

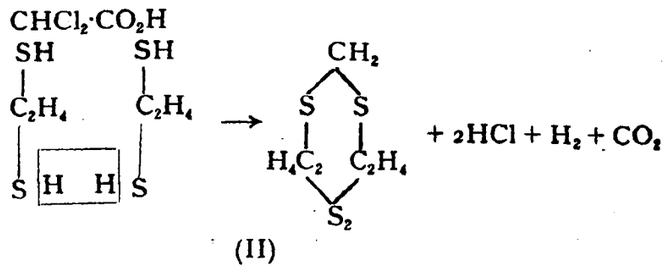
By Gopâl Chandra Chakravarti and Jogendra Mohan Saha.

The interesting physical and chemical properties possessed by triethylene tri- and tetrasulphides (Rây, *J. C. S.*, 1920, **117**, 1090; 1922, **121**, 1207) and benzylidene diethylenetri- and tetrasulphides (Rây, *J. C. S.*, 1924, **125**, 1141) led the present authors to undertake a more detailed investigation of a further series of cyclic polysulphides and their derivatives. It was anticipated that the reaction between dichloracetic acid and dithioethylene glycol would take the following course:—



(I)

resulting in the formation of the polysulphide (I). When, however, a mixture of equimolecular quantities of the acid and the mercaptan was either heated on the water-bath or gently boiled on the sand-bath, a compound with the composition, $C_5H_{10}S_4$, was isolated. The reaction can evidently be expressed in the following manner:—



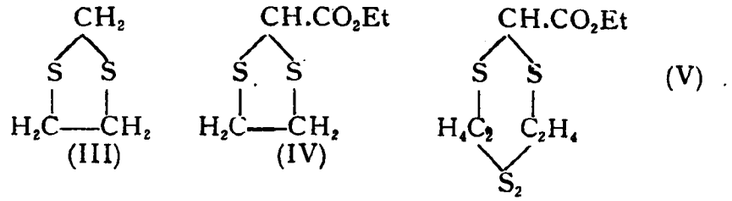
(II)

No reaction takes place if benzene is used as the solvent. But when dichloracetic acid and ethylene mercaptan are heated in xylene solution three isomeric compounds are obtained: one melting at 192–194°, another melting at 83–84° and the third, a liquid, all having the empirical formula $C_3H_6S_2$, which is the cyclic polysulphide (III).

[1] Reprinted from the *Journal of the Indian Chemical Society*, 1928, **5**, 453.

It is extremely probable that the above compounds represent different polymerides of (III).

Ethyl dichloracetate and potassium dithioethylene glycol gave rise to two different oily products which conform to the formulae (IV) and (V).



(V)

The compound (V) was formed in small quantities only. Attempts were therefore made to convert compound (IV) successively into compounds (I) and (III) by the usual methods of hydrolysis and heating. But all attempts to obtain the latter failed owing probably to the difficulty in identifying the degradation products. The investigations of Rây (*loc. cit.*) and others (Fromm and Engler, *Ber.*, 1925, **58**, 1916, etc.) show that many of the cyclic polysulphides can exist in several polymeric forms. The failure to identify the product of hydrolysis and heating of compound (IV) as any of the compounds (III) must be ascribed to the production of other polymers. Even the simplest compound ethylene disulphide has been obtained in four or five polymeric forms (*vide* Experimental). The expected compound (I) was however obtained by the interaction of potassium dichloracetate and potassium dithioethylene glycol in alcoholic solution.

Trichloracetic acid reacted with ethylene mercaptan under various conditions. No cyclic polysulphide containing the acid residue was formed in any of these reactions, the trichloracetic acid molecule only functioning as the oxidising agent by converting the mercaptan into various polymeric disulphides, except in one case only when a crystalline compound, m.p. 95–96° identical with the compound (II) was formed. The formation of this compound goes to show that trichloracetic acid is first reduced to dichloracetic acid which then reacts with the mercaptan to give rise to the compound (II) thus:

$$CCl_3{\cdot}CO_2H+C_2H_4(SH)_2=CHCl_2{\cdot}CO_2H+C_2H_4S_2+HCl.$$

EXPERIMENTAL.

Interaction of Ethylene Mercaptan and Dichloracetic Acid.—Six grams of the mercaptan (2 mols.) and 9 grams of the acid (1 mol.) were heated together either on a water-bath or gently boiled on a sand-bath for several hours. Copious evolution of hydrochloric acid, carbon dioxide and sulphuretted hydrogen took place. The dark

violet mass solidified on cooling and was well-washed with dilute caustic alkali and then with water. The alkaline wash water on acidification gave a very scanty green precipitate, insufficient for purification and analysis. The brown residue was extracted three or four times with hot alcohol. The filtrate on concentration gave a crop of brownish needle-shaped crystals of pentamethylene tetrasulphide (II) which were recrystallised from alcohol until they became white, m.p. 96° (Found: S, 65·8; C, 29·83; H, 4·52. $C_5H_{10}S_4$ requires, S, 64·6; C, 30·3; H, 5·1 per cent.). The residue was then successively and separately extracted with acetone, benzene and nitrobenzene. The products obtained by evaporating the solvents were found to be polymers of ethylene disulphide.

Interaction of Ethylene Mercaptan and Dichloracetic Acid in Xylene Solution.—Four grams of the mercaptan (2 mols.) and 6 grams of the acid (1 mol.) were heated together in 30 c.c. of xylene for about 29 hours. Evolution of hydrogen chloride, carbon dioxide and sulphuretted hydrogen took place. The solution was concentrated on the water-bath to about 10 c.c. and cooled. A granular crystalline precipitate was obtained. This was filtered, washed with cold alcohol and repeatedly crystallised from hot xylene. Fine yellow granular crystals of trimethylene disulphide (III), m.p. 192–194° soluble in benzene were obtained (Found: C, 34·3; H, 6·4. $C_3H_6S_2$ requires C, 33.96; H, 5·6 per cent.).

The filtrate after the separation of the yellow substance was dissolved in benzene and well washed with dilute caustic alkali and water. It was then filtered, dried with fused calcium chloride, again filtered and then evaporated. An oil mixed with a crystalline substance was obtained. The oil was extracted with a small quantity of ether leaving the white crystalline residue. After filtration the ether was driven off and the oil again extracted with a small quantity of ether. Finally on evaporation the ethereal solution gave a slightly brown, heavy oil with a sweet odour (Found: C, 34·2; H, 4·6; S, 61·38. $C_3H_6S_2$ requires C, 33·96; H, 5·6; S, 60·38 per cent.).

The white crystalline mass mentioned above was repeatedly crystallised from large amounts of ether in which it is very sparingly soluble. White granular crystals, m.p. 83–84° were obtained (Found: C, 33·51; H, 4·98. $C_3H_6S_2$ requires C, 33·96; H, 5·6 per cent.).

In the above reaction the yield of the yellow product was the largest whilst the other two were formed in small quantities only.

Interaction of Ethyl Dichloracetate and Monopotassium Ethylene Mercaptan.—The potassium salt (9 gms.), the ester (5·5 gms.) and

50 c.c. of anhydrous alcohol were refluxed together for about 5 hours. The solution was filtered hot from the solid precipitate of potassium chloride, evaporated to dryness and the residue extracted with benzene. The benzene solution was first shaken with dilute caustic alkali and then with water, filtered, dried, again filtered and the benzene removed. The oil thus obtained was repeatedly extracted with cold alcohol or ether. The residual oil was dissolved in benzene, filtered and evaporated to dryness when a brownish thick odourless oil was left. This is ethyl diethylene tetrasulphido-acetate (V) (Found: S, 47·27; C, 34·35; H, 5·94. $C_8H_{14}O_2S_4$ requires S, 47·41; C, 35·55; H, 5·19 per cent.).

The ethereal solution was evaporated to dryness and the residue extracted with a small quantity of ether leaving some insoluble oily and solid matters. The solution was evaporated and the previous process repeated several times until at last a transparent thick oil, ethyl ethylene disulphido-acetate (IV), with a pleasant odour was obtained (Found: C, 39·8; H, 5·89; S, 35·34. $C_6H_{10}O_2S_2$ requires C, 40·4; H, 5·6; S, 36·0 per cent.)

This oil was formed in larger amount in comparison with the previous one. It was dissolved in absolute alcohol and boiled with the calculated quantity of alcoholic potash for about two hours. The whole mass was evaporated to dryness and the residue dissolved in water and acidified with dilute hydrochloric acid. The turbid liquid was extracted with benzene and the benzene extract evaporated to dryness. The percentage of sulphur in this acid shows that it is most probably ethylene-disulphido-acetic acid (I), with which its properties correspond (Found: S, 41·95. $C_4H_6O_2S_2$ requires S, 42·66 per cent.).

Interaction of Potassium Dichloracetate and Monopotassium Ethylene Mercaptan.—Potassium dichloracetate (4·25 gms.), potassium mercaptide (4·75 gms.) and anhydrous alcohol (50 c.c.) were refluxed together for about an hour and filtered hot from the precipitate of potassium chloride. The filtrate was evaporated to dryness and the solid residue dissolved in water, filtered and acidified with concentrated hydrochloric acid in the cold and the turbid solution extracted with benzene. The benzene solution was well washed with water, filtered, dried and again filtered and evaporated to dryness. The oil thus obtained was purified by a repetition of the processes of extraction with a small amount of ether, filtration and evaporation—every time leaving some brown amorphous residue. A heavy oil (I) of pungent odour, insoluble in petroleum ether was obtained. It is strongly acid to litmus and decomposes alkali carbonates and bicarbonates (Found: C, 32·37; H, 4·7. $C_4H_6O_2S_2$ requires C, 32·00; H, 4·00 per cent.).

The oily acid was neutralised by the required quantity of pure caustic potash solution, the solution evaporated to dryness and the

residue crystallised from alcohol. The *potassium salt* was obtained as a colourless mass (Found: K, 19·63. $C_4H_5O_2S_2K$ requires K, 20·0 per cent.).

Interaction of Ethyl Trichloracetate and Ethylene Mercaptan.—The mercaptan (10 gms.) and the ester (10 gms.) were gently heated together for several hours on the sand-bath. Copious evolution of hydrochloric acid and sulphuretted hydrogen was noticed. The cold solid mass after washing with dilute alkali and water, was separated into different fractions by treatment with alcohol, chloroform, xylene and nitrobenzene. The products obtained from these solvents were amorphous and found to be polymerised ethylene disulphide. The ester was subsequently heated with the monopotassium salt of the mercaptan and also with its disodium salt in alcoholic and in benzene solutions—but only the polymers of ethylene disulphide were obtained. Next the monopotassium salt was shaken in the cold; ethylene disulphide was the only product.

Interaction of Trichloracetic Acid and Ethylene Mercaptan.—The mercaptan (10 gms.), the acid (9 gms.) and xylene (40 c.c.) were heated together for about 22 hours (benzene was first employed but no reaction ensued even on continued boiling) on the sand-bath. Evolution of large quantities of hydrochloric acid, carbon dioxide and sulphuretted hydrogen gases took place. The solution was evaporated to dryness and well washed with dilute alkali and then with water. The alkaline filtrate on acidification yielded no precipitate. The residue was refluxed with alcohol, filtered and the solution concentrated. Fine needle-shaped crystals with a slight greenish tinge were obtained. These were purified by repeated crystallisation from alcohol. White needles, m.p. 95–96° identical with the compound (II) derived from dichloracetic acid and ethylene mercaptan were obtained (*vide supra*). The residue after extraction with alcohol was separated into three fractions by refluxing with benzene, xylene and nitrobenzene respectively, but the products obtained from these solutions were all amorphous compounds, identical with the polymers of ethylene disulphide.

In conclusion, the authors take this opportunity of expressing their gratefulness to Sir P. C. Rây for his kind interest and help in this investigation.

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