

CCXVII.—*The Oxidation of Some Benzyl Compounds of Sulphur. Part I.*

By JOHN ARMSTRONG SMYTHE.

In a recent paper describing the preparation and reactions of benzyl tri- and tetra-sulphides (Smythe and Forster, *Trans.*, 1910, **97**, 1195), it was stated that both of the compounds are oxidised by hydrogen peroxide. The study of these reactions has led to some unexpected results, the investigation of which is still in progress. Meanwhile, a number of the benzyl compounds of sulphur have been submitted to the action of hydrogen peroxide in the hope that, thereby, some light would be thrown on the main problem, and the results of this work are embodied in the present communication.

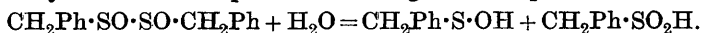
The compounds studied so far are the sulphide, sulphoxide, sulphone, disulphide, disulphoxide, and mercaptan of benzyl, and the mixed sulphide, benzoyl benzyl sulphide. Of these, only the sulphone is stable in contact with hydrogen peroxide. The sulphide is quantitatively oxidised to the sulphoxide or the sulphone, according to the amount of oxidising agent present, and the sulphoxide is converted into the sulphone.

In marked contrast to these monosulphidic compounds are those which contain two, three, or four atoms of sulphur linked together. Oxidation of such compounds always results in rupture, to a certain extent, of the sulphur atoms, and in the formation of benzaldehyde and the monosulphidic compounds, sulphuric and benzyldisulphonic acids. There is, however, a limit to the degree of rupturing possible, for it is found that the amount of sulphuric acid formed in the reaction is approximately constant, although the other products may vary in quantity to a considerable extent.

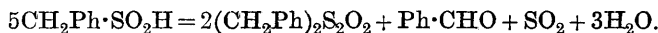
To take an example, benzyl disulphide gives on oxidation benzyl disulphoxide, benzaldehyde, sulphuric and benzyldisulphonic acids. The yields of disulphoxide in four experiments were 12, 56, 64, and 72 per cent. of the weight of material oxidised, and the yields of sulphuric acid, calculated on the disulphide, completely oxidised, that is, beyond the disulphoxide stage, were 17.7, 13.5, 13.1, 16.8 per cent. respectively.

In seeking for an explanation of this behaviour of the disulphide, two facts appear of importance; first, that the attainment of the full valency of the sulphur in the benzyl compounds is only possible in the case of the monosulphide; secondly, that the disulphoxide has been shown by Fromm and Palma (*Ber.*, 1906, **39**, 3308) to be capable of hydrolytic decomposition. We may conceive, then, the

first stages of the reaction between benzyl disulphide and hydrogen peroxide to consist in the oxidation to disulphoxide and the hydrolysis of this compound according to the equation:

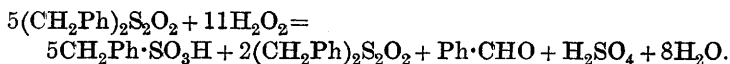


One of the products of hydrolysis, namely, the compound $\text{CH}_2\text{Ph}\cdot\text{S}\cdot\text{OH}$, has never been isolated, although its transient existence has been postulated by a number of chemists (for example, Fromm and Smiles). It would probably be immediately oxidised by hydrogen peroxide to benzyldisulphonic acid, $\text{CH}_2\text{Ph}\cdot\text{SO}_3\text{H}$. The other product, benzyldisulphinic acid, has been studied by Fromm and Palma, who were unable to analyse it owing to its instability. The substance was found to decompose spontaneously, especially in acid solutions, into benzyl disulphoxide, benzaldehyde, and sulphur dioxide. The probable equation expressing this decomposition is, according to Fromm and Palma (*loc. cit.*):



In the presence of hydrogen peroxide, sulphur dioxide would be immediately oxidised to sulphuric acid. This series of reactions would, therefore, account in a simple manner for all the products of oxidation of benzyl disulphide, and, as will be seen later, of the disulphoxide, mercaptan, and benzoyl benzyl sulphide as well.

This hypothesis may also be developed from the quantitative side. Summing up all the individual equations, the reaction between the disulphoxide and hydrogen peroxide may be represented thus:

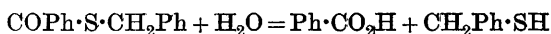


Of the five molecules of disulphoxide, two are thus regenerated, and the summation of an infinite number of cycles of such reactions yields the result that $8\frac{1}{3}$ gram-molecules of sulphonc acid and $1\frac{2}{3}$ gram-molecules of sulphuric acid are producible from 5 gram-molecules of the disulphoxide (or its equivalent of disulphide, mercaptan, etc.). The yield of sulphuric acid in the oxidation of these compounds can thus be calculated; it amounts to 13.2 per cent. in the case of the disulphide, 13.1 per cent. for the mercaptan, and 7.2 per cent. for the benzoyl benzyl sulphide.

The mean value found for the disulphide was 15.2; four determinations made in the case of the mercaptan gave the values 12.4, 14.3, 13.4, and 12.6, the mean of which is 13.2; and two determinations in the case of the benzoyl compound gave 6.8 and 8.4 per cent. (mean 7.6). When the experimental difficulties are borne in mind, the agreement is fairly satisfactory, and gives some support to the hypothesis.

The reaction between benzyl mercaptan and hydrogen peroxide affords an excellent example of step-wise oxidation, benzyl disulphide, benzyl disulphoxide, and benzyldisulphonic acid being successively formed. The two solids crystallise out in turn, evolution of heat accompanying the production of each compound. From the course of the reaction it is evident that the sulphonic acid is derived, in part at least, from the disulphoxide. The possibility of direct oxidation of the mercaptan to sulphonic acid would seem to be excluded in view of the large amount of sulphuric acid formed in the reaction; the yield of this being, as pointed out above, almost the same as that obtained from an equivalent weight of benzyl disulphide.

The substitution of a benzyl by a benzoyl group in the monosulphide does not favour the production of benzaldehyde by oxidation, for the chief product in the oxidation of benzoyl benzyl sulphide is benzoic acid. The amount of this and the rapidity with which it is formed leave no doubt that it is a primary product, and not the result of the oxidation of benzaldehyde initially formed. The other products of reaction are benzyldisulphonic acid, sulphuric acid, benzaldehyde, and benzyl disulphoxide—all compounds resulting from the oxidation of benzyl mercaptan. There can be no doubt, then, that the benzoyl compound behaves as an ester, being first hydrolysed as shown by the equation:



and that the mercaptan thus set free is oxidised as already described.

Reviewing briefly the results of this investigation, one sees in these reactions, carried out with similarly constituted compounds and under similar conditions, a two-fold tendency at work, namely, the striving of the sulphur atom to become fully oxidised, and its inability to become so, in the polysulphidic combinations, with resulting rupture of the molecule and degradation into monosulphidic compounds. From a consideration of the facts which are being slowly accumulated on this subject, it would appear that the reason for this inability is, in part at least, steric, but this cannot be stated definitely in the present state of our knowledge.

EXPERIMENTAL.

The method used throughout the course of this work is, with few slight modifications, the following. From 5 to 10 grams of the compound to be studied are dissolved in 20 to 100 c.c. of glacial acetic acid, and a measured volume of hydrogen peroxide solution (30 per cent.) is added. The reaction sometimes starts quickly

with considerable development of heat, sometimes so slowly as not to be perceptible, and in all cases without evolution of oxygen. The solid products crystallise out in part and are collected, and the liquors are deprived of excess of acetic acid by keeping in a vacuum desiccator over solid potassium hydroxide, small quantities of water being added from time to time to complete the precipitation of solid matter. The residual liquors from these operations are either warmed and treated with barium carbonate, the barium sulphate produced being determined and the barium benzylsulphonate obtained by crystallisation, or they are distilled in a current of steam and the benzaldehyde in the distillate is identified and determined by precipitation with phenylhydrazine. The determination of benzaldehyde by this method has but little quantitative significance, as control experiments show that the aldehyde is oxidised by hydrogen peroxide under the conditions in which it formed, the loss amounting on the average to 60 per cent. The sulphate determinations are more accurate, especially when the amount of hydrogen peroxide used is such that little or none remains after the completion of the reaction.

Benzyl Sulphide.—The reaction of this compound with hydrogen peroxide is rapid, and accompanied by considerable disengagement of heat; 5 grams of the sulphide and one equivalent of the peroxide yielded 5 grams of benzyl sulfoxide, melting after recrystallisation at 134° . Beyond a trace of sulphuric acid in the liquors, there are no secondary products of this reaction. (Found, $S=13.69$. $C_{14}H_{14}OS$ requires $S=13.94$ per cent.)

With excess of hydrogen peroxide (4 equivalents) oxidation of the sulphide is carried a stage further, benzyl sulphone being formed. Five grams of the sulphide yielded 5 grams of oxidation products, consisting largely of the sulphone with a small amount of sulfoxide. The sulphone, purified by crystallisation, melted at 151° . (Found, $S=13.03$. $C_{14}H_{14}O_2S$ requires $S=13.04$ per cent.)

The oxidation of benzyl sulphide with hydrogen peroxide is thus a very simple process, the sulfoxide or sulphone being formed quantitatively according to the amount of oxidising agent present. It is all the more remarkable, in view of this simplicity, that error should have crept into the literature of this subject. Hinsberg (*Ber.*, 1908, **41**, 2838) could find no trace of benzyl sulphone among the oxidation products of the sulphide, even when excess of hydrogen peroxide was employed, and on this alleged fact is founded an argument in favour of the symmetrical constitution of the disulphoxides. Prominence has further been given to the error, although unwittingly on the part of the authors, in a recent publication by Fichter and Wenk (*Ber.*, 1912, **45**, 1373).

Benzyl Sulphoxide.—As might be expected from the foregoing reaction, this compound is readily oxidised to benzyl sulphone. Five grams of sulphoxide and 10 c.c. of hydrogen peroxide in the presence of 25 c.c. of acetic acid yielded 5.2 grams of benzyl sulphone, melting at 151° . (Found, S=12.89. $C_{14}H_{14}O_2S$ requires S=13.04 per cent.) There was no appreciable liberation of heat, and no secondary products were detected.

Benzyl sulphone is quite unaffected by hydrogen peroxide, even after prolonged heating to 100° ; it can be quantitatively recovered from the solution, which contains the merest trace of sulphuric acid.

Benzyl Disulphide.—The oxidation of this compound by hydrogen peroxide, in acetic acid solution, was studied by Hinsberg (*Ber.*, 1908, **41**, 2839), who presumably isolated the disulphoxide from the solid products of reaction. The liquors from these were stated, by this author, to contain small quantities of a compound with a lower melting point than the disulphoxide. This was possibly unaltered disulphide.

The reaction frequently sets in suddenly, especially if the materials are well shaken. Sometimes two distinct phases of oxidation can be detected, one corresponding with the crystallisation of disulphoxide, the other to the passing of this into solution, and each is accompanied by the liberation of heat. The products of reaction are benzyl disulphoxide (m. p. 108° ; Found, S=23.10. $C_{14}H_{14}O_2S_2$ requires S=23.06 per cent.), benzyisulphonic acid (Found, Ba in barium salt=26.56; $(C_7H_7\cdot SO_3)_2Ba\cdot 2H_2O$ requires Ba=26.60 per cent.), sulphuric acid, and benzaldehyde.

Minute quantities of an evil-smelling substance, which clings obstinately to the disulphoxide during crystallisation, but is destroyed, apparently with the liberation of sulphur, by prolonged warming of the solution, are also produced in this reaction. The relative quantities in which the products are formed depends on the amount of oxidising agent present. With one equivalent of hydrogen peroxide, the yield of disulphoxide is 78 per cent., and but little sulphonic acid is produced; with three equivalents of hydrogen peroxide, only 12 per cent. of disulphoxide is formed, but the yield of sulphonic acid rises to 60 per cent. The yield of benzaldehyde varies from 6 to 9 per cent.; that of sulphuric acid is, on the average, 15 per cent. of the weight of disulphide taken.

Benzyl Disulphoxide.—This is oxidised very slowly in the cold, possibly by reason of its sparing solubility. If the reaction is started by gently warming, it proceeds with vigour. The products are benzyisulphonic acid, sulphuric acid, and benzaldehyde. On one occasion, minute quantities of a solid melting at 170° were

obtained, but the amount was too small for analysis, and subsequent attempts to prepare it failed. The yield of benzaldehyde is about 3 per cent., and of sulphuric acid 11 per cent. In one experiment, 5 grams of the disulphoxide furnished 7.6 grams of pure barium benzylsulphonate (Found, $\text{Ba}=26.6$. $(\text{C}_7\text{H}_7\cdot\text{SO}_3)_2\text{Ba}\cdot 2\text{H}_2\text{O}$ requires $\text{Ba}=26.6$ per cent.), which corresponds with a yield of 92 per cent. of the free acid. The maximum yield in terms of the hypothesis sketched in the introduction is 102 per cent.

Benzoyl Benzyl Sulphide.—The behaviour of this mixed sulphide with hydrogen peroxide is very different from that of the dibenzyl sulphide, for, as already mentioned, the evidence all points to primary hydrolysis followed by oxidation of the mercaptan, which is one of the decomposition products. The method of working adopted is somewhat different from the ordinary one, and may be illustrated by briefly recounting the procedure in one experiment.

Five grams of the compound were dissolved in 25 c.c. of acetic acid, and 5 c.c. of hydrogen peroxide added. The solution became warm after an hour's interval, and remained warm for over an hour. Next day, the excess of acetic acid was removed by evaporation over potassium hydroxide, water added, and the liquid extracted with ether. The aqueous portion was treated with barium carbonate, filtered from the excess of this reagent and barium sulphate, and the soluble salt obtained by crystallisation from the filtrate. This proved to be barium benzylsulphonate. (Found, $\text{Ba}=26.65$. $(\text{C}_7\text{H}_7\cdot\text{SO}_3)_2\cdot 2\text{H}_2\text{O}$ requires $\text{Ba}=26.60$ per cent.)

The ethereal portion was washed with sodium carbonate solution and allowed to evaporate. It deposited about 1 gram of unaltered benzoyl compound (m. p. 38°), and a small amount of acicular crystals melting at 108° . A mixed melting-point determination proved this substance to be benzyl disulphoxide, whilst benzoic acid was obtained from the alkaline extract (m. p. 121° ; Found, Ag in silver salt = 47.30. Calc., Ag = 47.15 per cent.).

The yields of the various products obtained in other trials were: benzoic acid, 43 per cent.; benzaldehyde, 1 and 2 per cent.; sulphuric acid, 6.8 and 8.4 per cent.

Benzyl Mercaptan.—There are three distinct stages in the oxidation of the mercaptan by hydrogen peroxide. The solution quickly becomes warm, then an emulsion is formed, and crystals separate after about fifteen minutes. In the next stage, these crystals dissolve, more heat is developed, and fresh crystals appear; this stage occupies about an hour. Finally, the crystals pass slowly into solution, and at the end of a few days the liquid is clear again. The solid produced in the first stage of reaction melts, after purification, at 71° , and is benzyl disulphide (Found, $\text{S}=25.83$;

$C_{14}H_{14}S_2$ requires $S=26.07$ per cent.); that formed in the second stage melts at 108° , and is benzyl disulphoxide. (Found, $S=22.90$; $C_{14}H_{14}O_2S_2$ requires $S=23.03$ per cent.)

The clear solution, worked up in the usual way, yields barium benzyisulphonate. (Found, $Ba=26.60$. $(C_7H_7 \cdot SO_3)_2Ba, 2H_2O$ requires $Ba=26.60$ per cent.)

The yield of the sulphonic acid amounts (with four equivalents of hydrogen peroxide) to 72 per cent.; of benzaldehyde, from 7 to 14 per cent.; of sulphuric acid, 13 per cent. With deficiency of hydrogen peroxide (two equivalents), the yield of sulphonic acid is small, whilst that of disulphoxide rises to 48 per cent.

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ARMSTRONG COLLEGE,
NEWCASTLE-ON-TYNE.
