Reactions of Ethyl Disulphide and Alkyl Iodides in Presence of Mercuric Iodide

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INTRODUCTION

The purpose of this work was partly to clarify reactions of simple compounds containing sulphur and having analogy to wool keratin, and partly to attempt transferring these reactions to wool. The wool keratin has a unique position among the proteins owing to the high sulphur contents, which amount to 3—4 % and are of the greatest importance for the properties of wool.

In keratin the main peptide chains are linked together laterally by sulphur in the cystin. The bridges between the chains, the disulphide bonds, are relatively easily attacked. If therefore the disulphide bond could be transformed into a more stable bond by chemical means, an improvement in the resistance of wool to attack might result. Several attempts have been made but so far with only limited success.

In the first part of the investigations ethyl disulphide was used, the reactions with alkyl iodide and alkylene diiodide in presence of mercuric iodide being examined.

THEORETICAL

Hilditch and Smiles¹ have described reactions of ethyl disulphide and ethyl iodide in presence of mercuric iodide and state that they have been able to isolate some unknown intermediate reaction products. In spite of a most careful investigation it has been impossible to reproduce these compounds.

The reaction of ethyl disulphide and ethyl iodide gives the following products in 2—3 months:

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The said authors suppose that the reaction passes through the following stage:

and that the thioethyl group subsequently is split off and replaced by an ethyl group with liberation of iodine. The intermediate product — diethyl thioethyl sulphonium iodide — should be impossible to isolate in this case as it is rapidly converted into triethyl sulphonium iodide.

If, however, mercuric iodide is present in the reaction mixture, the velocity of the addition is considerably increased, and by interrupting the reaction after a certain time, the authors are of the opinion that they had isolated diethyl thioethyl sulphonium iodide as a double salt with mercuric iodide (3). By prolonged action Hilditch and Smiles found triethyl sulphonium iodide with one or two molecules mercuric iodide, (5) and (4), and liberated iodine.

Reagents	Time	Main product	
Equimolecular proportions of ethyl disulphide and mercuric iodide	12 hours	$(\text{C}_2\text{H}_5)_2(\text{C}_2\text{H}_5\text{S})\text{SJ} \cdot 2\text{HgJ}_2$	(3)
with excess of ethyl iodide.	3 days	$(\text{C}_2\text{H}_5)_3\text{SJ} \cdot 2\text{HgJ}_2$	(4)

Some of the experimental data from the paper are compiled, *viz.*: the melting points and the combustion analyses of the alleged intermediate (3) and the final products (4) and (5), and the theoretical values for carbon and hydrogen in the said compounds.

(3)	$\text{C}_6\text{H}_{15}\text{Hg}_2\text{J}_5\text{S}_2$	(1187)	M.p.	104° C	Calc.	C	6.07	H	1.274
					Found	»	5.88	»	1.19
(4)	$\text{C}_6\text{H}_{15}\text{Hg}_2\text{J}_5\text{S}$	(1155)	M.p.	115—116° C	Calc.	»	6.239	»	1.309
					Found	»	6.44	»	1.31
(5)	$\text{C}_6\text{H}_{15}\text{HgJ}_3\text{S}$	(700)	M.p.	110° C	Calc.	»	10.29	»	2.14
					Found	»	10.40	»	2.03

By calculating the discrepancy between the values found for (3) and the theoretical values for (4) in percent, it gives the differences: C = -5.75%, H = -9.09%. Due to the low contents of carbon and hydrogen the possibility can not be excluded that the authors have analysed an impure triethyl sulphonium compound.

A thorough investigation by the present author has shown that it is impossible to isolate the intermediate diethyl sulphonium iodide even in presence of mercuric iodide. It appears most probable that the sulphur-sulphur bond in the disulphide is split and that the thioethyl groups immediately form the triethyl sulphonium iodide (6).

The experiments were carried out with ethyl disulphide, mercuric iodide and the following iodides: 1) Ethyl iodide; 2) methyl iodide; 3) *n*-propyl iodide; 4) *n*-butyl iodide; 5) trimethylene diiodide. All the monoiodides reacted according to equation (6). The velocity of reaction varied with the different iodides. With methyl iodide the velocity was greatest, in 2—3 hours the mercuric iodide was dissolved, and the first crystals could be isolated after only 1 hour. With ethyl iodide crystals were isolated after 10—14 hours, whereas the reaction with *n*-propyl iodide took considerably more time.

The symmetrical triethyl sulphonium iodide was most readily obtained as crystals. From the reaction mixture with methyl iodide as well as from that with *n*-propyl iodide yellow oils first separated. These oils crystallized after being kept for some time, and the crystalline products were easily purified. The product of the reaction with *n*-butyl iodide did not crystallize — even on sharp cooling. With trimethylene diiodide a yellow oil was first precipitated, from this a yellow powder separated. The powder was completely insoluble in all common solvents and could accordingly not be recrystallized.

In the cases where crystalline compounds were formed, analyses of the products were made. In every case it was shown that the crystals first formed were identical with those precipitated at a later stage. In none of the experiments a thioethyl compound could be isolated, but respectively:

$(C_2H_5)_3SJ \cdot HgJ_2$	melting point	110° C
$(C_2H_5)_3SJ \cdot 2HgJ_2$	» »	115—116° C
$(CH_3)_2(C_2H_5)SJ \cdot HgJ_2$	» »	84—85° C
$(n-C_3H_7)_2(C_2H_5)SJ \cdot HgJ_2$	» »	74—75° C

With trimethylene diiodide the reaction takes a course different from that of the monoiodides. A comparison between the found composition (see Exp.) and some theoretical values shows a poor agreement. The high contents of iodine found indicate that — at least to some extent — only one of the iodine atoms of the trimethylene diiodide has reacted, possibly in conjunction with some chain or ring formation. The high melting point — the product did not melt at 350° C — may likewise be taken as suggesting a high molecular weight.

EXPERIMENTAL

1) *Ethyl iodide*. Equivalent portions of ethyl disulphide and mercuric iodide were weighed and about three times the calculated amount of ethyl iodide was added, acetone being used as a solvent. In some cases the excess of ethyl iodide used was sufficient to act as a solvent in itself.

The mixture was shaken continuously at room temperature and the time of reaction varied from a few hours to several days. In all cases the reaction mixture turned brown

after a few hours, the reaction proceeding most rapidly with ethyl iodide as a solvent. Undissolved mercuric iodide was filtered off and the brown solution which contained iodine was decolorized with charcoal. On addition of ether yellow needles were precipitated, these were recrystallized in different ways: a) By cooling a hot, saturated acetone solution; b) by precipitating from an acetone solution by means of ether; c) by precipitating from an acetone solution by means of water; d) by cooling a hot, saturated solution in ethyl alcohol; e) by cooling a hot, saturated solution in methyl alcohol.

In all cases the melting point of the product was 110°C , whether the mixture had reacted for 10–14 hours or for several days. This product should be the compound: $(\text{C}_2\text{H}_5)_3\text{SJ} \cdot \text{HgJ}_2$ (5), and the analysis corroborates this.

By using two equivalents of mercuric iodide in relation to the ethyl disulphide, the crystals separating were of a stronger yellow hue. They were easily decomposed by treatment with ether, and were therefore purified by concentrating the acetone solution *in vacuo*. The substance melted at $115\text{--}116^{\circ}\text{C}$ with separation of mercuric iodide. These crystals correspond to the composition: $(\text{C}_2\text{H}_5)_3\text{SJ} \cdot 2\text{HgJ}_2$ (4).

The crystals most readily formed, whether produced in a short or a long time, melt at 110°C , irrespective of the way in which they have been purified. Pure crystals of m.p. 104°C have been impossible to obtain. With different combinations of (4) and (5) the melting points are lower than for either of them. A 1 : 1 mixture melted at 90°C whereas all other mixtures gave melting points between 90 and 115°C .

Iodine was estimated according to Baubigny-Chavanne².

Mercury was estimated in two ways: 1) By conductometric titration with sodium sulphide. The substance was dissolved in acetone and water added till near precipitation. A calculated amount of silver nitrate was added and the very slightly soluble silver iodide was filtered off. The solution was diluted with water to appr. 200 ml and titrated with 0.5 *N* sodium sulphide. The method gives distinct equivalent points. 2) By digestion and weighing as mercuric sulphide according to Rupp-Nöll³.

(4) $\text{C}_6\text{H}_{15}\text{Hg}_2\text{J}_5\text{S}$ (1155) M.p. $115\text{--}116^{\circ}\text{C}$	Calc.	Hg 34.74	J 54.95
	Found	» 34.80 (method 2)	» 54.96
(5) $\text{C}_6\text{H}_{15}\text{HgJ}_3\text{S}$ (700) M.p.	110°C Calc.	» 28.64	» 54.35
	Found	» 28.70 (method 1)	» 54.43
		» 27.96 (method 2)	»

The experimental methods as described for ethyl iodide were also used in the case of the other iodides.

2) *Methyl iodide*. By precipitating with ether a yellow oil first separated which crystallized in the course of a few minutes.

After purification the crystals were needleshaped, m.p. $84\text{--}85^{\circ}\text{C}$.

$\text{C}_4\text{H}_{11}\text{HgJ}_3\text{S}$ (672)	Calc.	C 7.14	H 1.65	Hg 29.80	J 56.61
	Found	» 7.25	» 1.58	» 28.60 (method 1)	» 56.55
				» 29.50 (method 2)	»

3) *n-Propyl iodide*. By precipitating with ether a yellow oil separated and from this oil large crystals were slowly formed.

They were easily purified by recrystallization, m.p. $74\text{--}75^{\circ}\text{C}$.

$\text{C}_8\text{H}_{19}\text{HgJ}_3\text{S}$ (728)	Calc.	C 13.19	H 2.63	Hg 27.54	J 52.25
	Found	» 12.43	» 2.66	» 26.82 (method 1)	» 52.70
				» 27.93 (method 2)	»

4) *n-Butyl iodide*. It was impossible to make the yellow oil formed crystallize and for this reason an analysis was not undertaken. The velocity of reaction according to

equation (6) was, however, determined in the same manner as for the other alkyl iodides.

5) *Trimethylene diiodide*. From the yellow oil precipitated on the addition of ether a yellow powder separated on standing. The product could not be recrystallized, because once precipitated, it could not be redissolved. It was thoroughly washed with acetone before the analysis was carried out.

Some theoretical values are calculated and compared with the found composition.

(a) $C_5H_{11}HgJ_3S$	(684)	Calc.	C	8.78	H	1.62	Hg	29.30	J	55.62
(b) $C_5H_{11}Hg_2J_5S$	(1139)	»	»	5.28	»	0.97	»	35.22	»	55.71
(c) $C_{10}H_{22}HgJ_3S_2$	(914)	»	»	13.1	»	2.42	»	21.93	»	55.50
(d) $C_8H_{17}HgJ_5S$	(980)	»	»	9.8	»	1.75	»	20.46	»	64.73
		Found	»	12.1	»	2.16	»	21.7	»	61.5

In (a), (b) and (c) are supposed that both, in (d) only one of the iodine atoms in trimethylene diiodide have reacted. The agreement is best for (c). But the high value of iodine contents as compared with the theoretical one in (a) and (b), may be taken to indicate that not all the iodine atoms in the trimethylene diiodide have reacted, and that some reaction according to (d) may have occurred.

Determination of the velocity of reaction of ethyl disulphide, mercuric iodide and alkyl iodides

From the equation:

it is seen that iodine is liberated in an amount equivalent to the sulphonium salt formed, and by determination of the iodine the amount reacted can be estimated. The iodine was determined by titration with standard sodium thiosulphate solution. As mentioned above, it turned out that the reaction proceeded most rapidly when alkyl iodide was used in such an excess that it acted as a solvent. During the reaction the mixtures were shaken continuously.

1 g ethyl disulphide and 7.5 g mercuric iodide were weighed and then mixed with 4–6 times the calculated amount of alkyl iodide in ground glass-stoppered flasks. The samples withdrawn were diluted with acetone and titrated with 0.1 N sodium thiosulphate solution (with samples containing much iodine, 0.2 N solution was used).

In the graph the results of the velocities may be compared.

Hilditch and Smiles¹ state that the reaction between ethyl iodide and dimethyl sulphide in presence of mercuric iodide is complete in 15 minutes. In comparison the reaction of ethyl iodide and ethyl disulphide appears rather slow, indicating that the reaction is of an other kind. Though the first crystals could be isolated after 10 hours reaction, the yield in 30 days was only 90 %.

Though the value for the liberated iodine are hardly sufficiently accurate to allow an exact analysis of the reaction, it is seen that the curves found can

Velocity of reaction by the formation of the five different sulphonium iodides, all of them with complex bound mercuric iodide.

- Dimethyl ethyl sulphonium iodide.
- Triethyl sulphonium iodide.
- +— Di-n-propyl ethyl sulphonium iodide.
- ▼— Di-n-butyl ethyl sulphonium iodide.
- ×— Product from trimethylene diiodide.

not easily be reconciled with the assumption of the formation of a comparatively stable intermediate product. Were namely a diethyl thioethylsulphonium compound first formed this reaction should take place without liberation of iodine, and the velocity of iodine formation should consequently increase from zero up to a certain point. In other words, a twostage reaction with a stable intermediate product should be indicated by a curve with a point of inflection.

Some of these reactions were carried out on wool, but in this case other groups, for instance the amino groups, can also react and cause complications. Investigations on the supercontraction of the wool fibers made it, however, possible to show some change in the disulphide links. The supercontraction of the fibers compared with increase in weight indicated that the disulphide bonds had reacted to some extent. Following cases were examined: a) Untreated wool; wool treated with b) mercuric iodide; c) methyl iodide and mercuric iodide; d) trimethylene diiodide and mercuric iodide; e) methyl iodide; and f) trimethylene diiodide.

SUMMARY

The intermediate compound diethyl thioethyl sulphonium iodide mercuric iodide described by Hilditch and Smiles could not be reproduced. By treating ethyl disulphide with 1) ethyl iodide in presence of mercuric iodide, only

triethyl sulphonium iodide with one and two molecules mercuric iodide were isolated. The formation of triethyl sulphonium iodide liberates iodine as stated by Hilditch and Smiles. According to equation (6) the reaction liberates one equivalent of iodine, which makes it possible to determine the velocity of the reaction. The present author made also experiments with ethyl disulphide and the following alkyl iodides: 2) Methyl iodide; 3) *n*-propyl iodide; 4) *n*-butyl iodide; and 5) trimethylene diiodide. The alkyl moniodides give dialkyl ethyl sulphonium iodide mercuric iodide. The products from methyl iodide and from *n*-propyl iodide were — like those from ethyl iodide — crystalline, and they were all analyzed. The product from *n*-butyl iodide did not crystallize.

It was impossible to clarify the reaction mechanism between ethyl disulphide and trimethylene diiodide, but the insoluble reaction product was analyzed.

The velocities of all reactions mentioned were determined and compared. Methyl iodide reacted most rapidly.

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