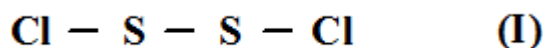


Chemical Composition and Structure of Sulphur Monochloride (S₄Cl₄)

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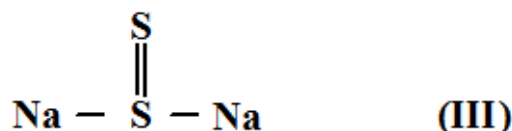
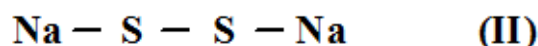
Abstract:

Keywords: sulphur mono chloride, structure, chemical composition, Vorozhtsov Sulphur mono chloride is one of the most usable substances in chemical industry. It is used in synthesis of medicine, dyes, additions and other substances, as well as a vulcanizer curing agent. However, its chemical composition and structure are not investigated completely. The structure of sulphur mono chloride is presented in scientific literature by the formula (I):



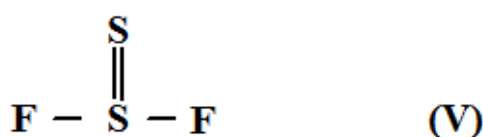
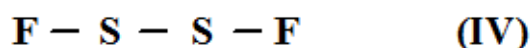
Nevertheless, the fact of colour presence in S₂Cl₂ by itself proves that the given structure seems to be incorrect, as according to the theory of color value (by O.Vitt, 1876) the composition of sulphur monochloride should contain a chromophore group (S=S) that imparts the colour to the substance. In addition to this, from the very beginning the formula of S₂Cl₂ denies the idea of being of the products of monochloride which boils between 59⁰C and 135⁰C.

In 1932 N.N. Vorozhtsov postulated for the first time the opportunity of existing Na₂S₂ as two isomeric forms: disulphide (II) and thiosulphide (III) [1]:

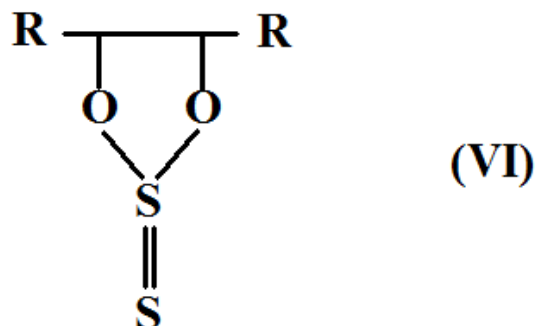


Later Price and Stacy [2], as well as Matsukawa, Ohta and Shirakawa [3] demonstrated that these samples of 4,4-dinitro-diphenyldisulphide obtained in reaction between 4-nitrochlorobenzene and Na₂S₂ were the eutectic mixture of the corresponding disulphide and sulphide. In addition to this, the real existence of compounds having thiosulphoxide structure (S=S<) was repeatedly noted in scientific literature. So, Steudel [4] has discovered at the temperatures below -100⁰C the stable sulphur modifications having structures of the type ...S-S (:S) S-S-...

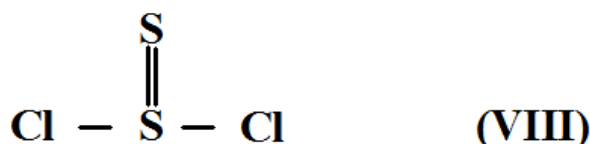
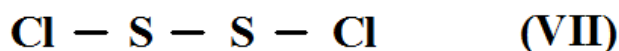
A bit earlier F. Seel [5,6] had shown that sulphur monofluoride was a mixture of two forms (IV, V) even at a usual temperature:



Kuczkovski [7,8] made a similar conclusion concerning the structure of this compound. The thiosulphide form (VI) was ascribed to the reaction products of some 1,2-glycols and sulphur monochloride [9]:

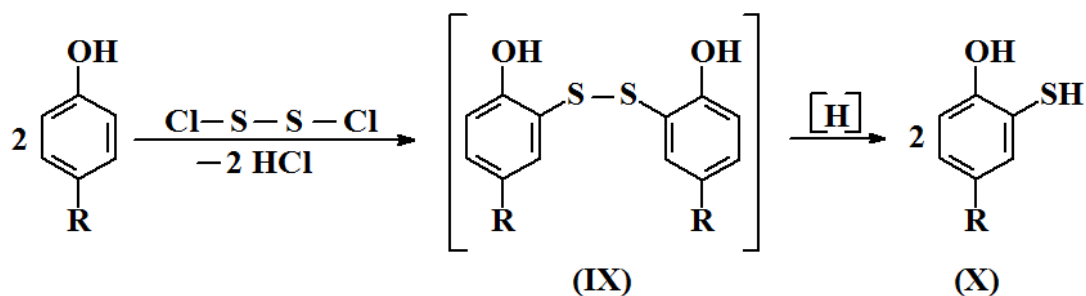


In 1974 V.I.Stepanov, V.I.Rodionov and T.A.Tchibissova [10] supposed that disulphide (VII) and thiosulphide (VIII) groups were also present in S₂Cl₂ composition:



Scientists pointed out that the problem has not only theoretical but also an applied character as the structure of sulphury dyes obtained from Na₂S₂ and S-S bounds was not ascertained enough in them [10].

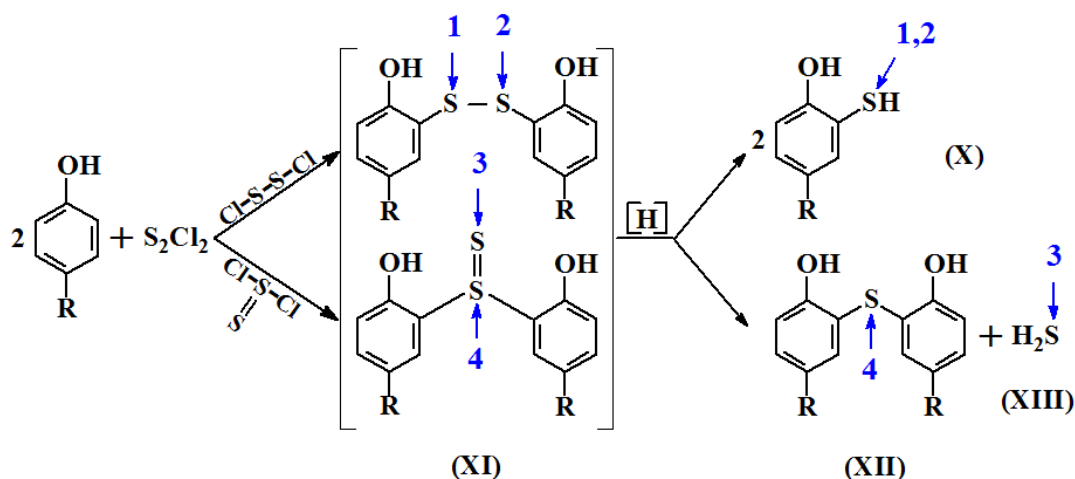
In 1976 A.M.Kuliev and his colleges [11] demonstrated the reaction of reducing disulphide (IX) obtained from reacting p-alkylphenol and sulphur monochloride:



In the process of reduction (IX) 1-hydroxy-2-thio-4-alkylcyclohexa triene-2,4,6 (X) has been synthesized and investigated, the yield being 31.3% [11]; the other reaction product yielding much more – 68.7%, has not been investigated and no information is available about it. In addition to it, the fact of hydrogen sulphide release in the process of reducing sulphide mass (IX) which production is not provided by the reaction scheme represented above has not been explained. The main thing is that no information is available about chromophore group of sulphide mass (IX) splitting.

All the investigations and assumptions cited above induced us to research the structure of sulphur monochloride more thoroughly.

Our investigations showed that if we have to accept the assumption that sulphur monochloride consists of two isomers (VII and VIII) [10], the sulphidation process and further disulphide and thiosulphide reduction should proceed according to the following scheme [12]:



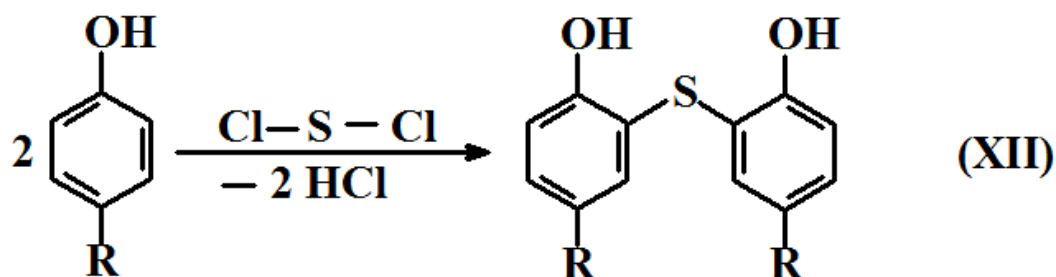
where R – CH_3 ; tret. – C_4H_9

As we see, in the process of reduction (XI) from the disulphide form: 1-hydroxy-2-thio-4-alkylcyclohexatriene-2,4,6; (X) and from the thiosulphide form: 2-thio-bis-(1-hydroxy-4-alkylcyclohexatriene-2,4,6) (XII) are synthesized with H_2S (XIII) (see the table below).

Table Compounds synthesized by reacting p-alkylphenol and sulphur monochloride and reducing tetrasulphide

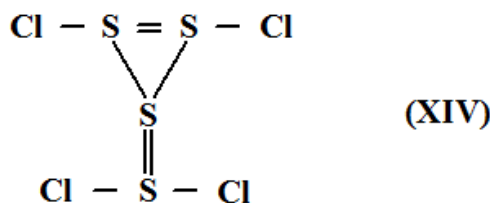
p-alkylphenol:sulphur monochloride ratio	Temperature, °C	Substance yield, %		
		(X)	(XII)	(XIII)
2:1	30			H_2S
		49	44,5	4,6

2-thio-bis-(1-hydroxy-4-alkylcyclohexatriene-2,4,6) (XII) has also been produced by counter-synthesis in reacting p-alkylphenols and SCl_2 :



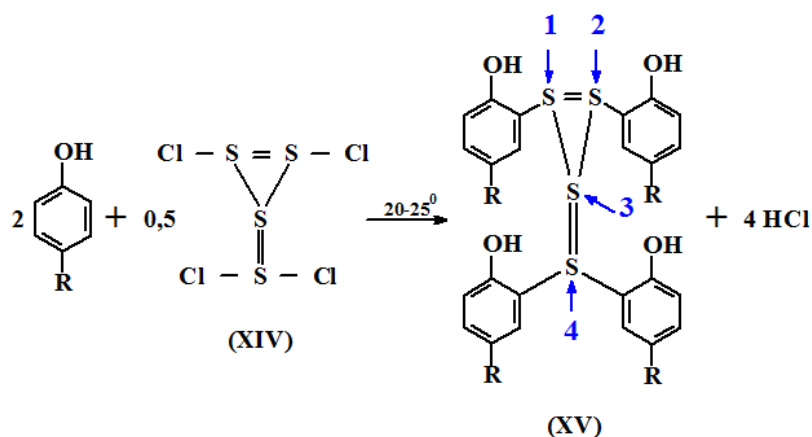
Thus, we prove the presence of disulphide (VII) and thiosulphide (VIII) groups in the structure of sulphur monochloride by means of experiment. But another problem has to be solved: Is it true that sulphur monochloride is in fact a mixture of these two isomers? In this case they will be separated by the boiling temperature.

Basing on the arguments given above, we are the first to postulate the assumption that only one structural form of sulphur monochloride exists. This structure combines disulphide and thiosulphoxide fragments (XIV) [13, 14]:

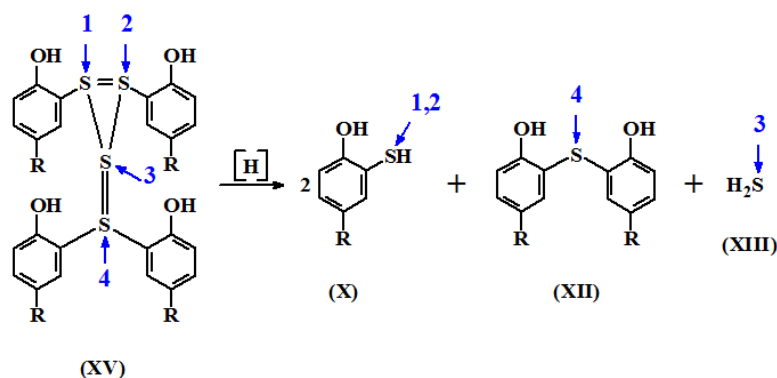


The given structure (XIV) above of sulphur monochloride is the most acceptable because it satisfies the requirements of the color value theory. From the other hand the reason of great difference between boiling temperatures of SCl_2 and sulphur monochloride (S_4Cl_4) becomes more evident as one extra atom of sulphur S_2Cl_2 cannot be the reason for such breaking ($59^\circ\text{C} - 135^\circ\text{C}$).

According to this structure (XIV) the p-alkylphenols sulphidation first results in the production of colored substances (XV) that has not been described in corresponding literature before:



The further reducing by zinc and hydrochloric acid of the indicated above colored substances (XV) leads to the complete chromophore group splitting that results in producing of 1-hydroxy-2-thio-4-alkylcyclohexatriene-2,4,6 (X), 2-thio-bis-(1-hydroxy-4-alkylcyclohexatriene-2,4,6) (XII) and hydrogen sulphide (XIII). The structure of the sulphidation products allows calculating theoretically the yield of each reduction product which includes sulphur atoms into their molecule. Thus, proceeding from the structure of the starting product of sulphidation, theoretically the yield of 1-hydroxy-2-thio-4-alkylcyclohexatriene-2,4,6 (X) should reach 50,2%. Practically this product output, as it was pointed out above, makes up 49%. Proceeding from the pointed formula (XV) the theoretical output of 2-thio-bis-(1-hydroxy-4-alkylcyclohexatriene-2,4,6) (XII) and hydrogen sulphide should not exceed 44,8% and 4,9% accordingly. Practically the yield of 2-thio-bis-(1-hydroxy-4-alkylcyclohexatriene-2,4,6) (XII) and hydrogen sulphide consists of 44,5% and 4,6% accordingly. It makes possible to assume that in the reduction process sulphur atoms 1 and 2 take part in producing a sulphhydryl group (X), a sulphur atom of 4 – sulphide group and 3 hydrogen sulphide. So, the theory is completely proved with the help of experiment. The reduction reaction may be represented by the following scheme:



Synthesis of the compounds: 1-hydroxy-2-thio-4-tret.-butylcyclohexatriene-2,4,6 (**X**), 2-thio-bis-(1-hydroxy-4-tret.-butylcyclohexatriene-2,4,6 (**XII**) and hydrogen sulphide (**XIII**) in the reducing process proves the chemical composition and structure of the substance (**XV**). The experimental confirmation of the chemical composition and structure of the substance (**XV**) in fact proves that the chemical composition and structure of substance (**XIV**) is right, that is sulphur monochloride (S_4Cl_4), which is mistakenly known as (S_2Cl_2) in science up to now.

Experimental Part

Synthesis of the compounds:

1-hydroxy-2-thio-4-tret.-butylcyclohexatriene-2,4,6 (X),
2-thio-bis-(1-hydroxy-4-tret.-butylcyclohexatriene-2,4,6 (XII) and
hydrogen sulphide (XIII).

150g of p-tret.-butylphenol was dissolved in 300 ml of benzene. Then, 67,5g of sulphur monochloride was dropwise added over a period of 60 minutes at a reaction temperature of 20-25°C. The reaction mixture was mixed during 40-60 minutes at a temperature of 70-75°C. Then the obtained tetrasulfide mass was reduced by atomic (Zn-HCl) hydrogen during 24 hours at a temperature of 10-20°C. The reduction process was conducted until the chromophore groups became completely splitted. The obtained substances were washed with hot water. Then the benzene was distilled off. The residue was distilled off in vacuum. The residue was distilled off in vacuum to obtain:

1-hydroxy-2-thio-4-tret.-butylcyclohexatriene-2,4,6 (X) as a transparent liquid; Boiling point: 85-86°C (0.3 mm). d_4^{20} 1.0740; n_D^{20} 1.5590; MR_d 54.79; calculated 54.86. Found %: C 65.67; H 7.85; S 17.65. $C_{10}H_{14}OS$. Calculated %: C 65.89; H 7.73; S 17.59.

2-thio-bis-(1-hydroxy-4-tret.-butylcyclohexatriene-2,4,6 (XII) as white crystals. The obtained substance (**XII**) was recrystallized in isooctane. Melting point: 92°C.

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