SOME INVESTIGATIONS ON POLY(SULPHUR OXIDE) AND ITS REACTION WITH SILICON TETRACHLORIDE

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SOME INVESTIGATIONS ON POLY(SULPHUR OXIDE) AND ITS REACTION WITH SILICON TETRACHLORIDE

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Poly(sulphur oxide) has been prepared by the low temperature thermal decomposition of the lower oxides of sulphur. This yellow, elastic solid resists water hydrolysis. It is unstable at room temperature when stored under vacuum and decomposes slowly to a powdery yellow white cyclic(sulphur oxide) and sulphur dioxide. In the presence of silicon tetrachloride, the thermal decomposition gives rise to an adduct of the lower oxide of sulphur along with the poly(sulphur oxide). The adduct hydrolyses to silica, hydrogen chloride, hydrogen sulphide and hydrogen sulphite. Based on the analysis of the hydrolysed products and the IR data, the adduct is assigned a formula of $SiCl_4 \cdot 2(SO)$, in which the silicon is hexacoordinated.

INTRODUCTION

In continuation of our work on silicon halides, we found that silicon tetrachloride reacts with a suboxide of sulphur. Poly(sulphur oxide) has been prepared by the low temperature thermal decomposition of lower oxides of sulphur. The lower oxide of sulphur has been prepared by the solid state reaction of cupric oxide and sulphur at 300–400°C in vacuum.[1] The poly(suphur oxide), yellow in colour and powdery in nature has been characterised by IR spectroscopy and elemental analysis. The analysis indicates a composition of $S_x O_y$ ([x = 7–8, y = 5–6]. This poly(sulphur oxide) during its formation is treated with silicon tetrachloride in chloroform. A part of the silicon tetrachloride forms an adduct with a species of a sub(sulphur oxide) and remains as a solid imbedded in the poly(sulphur oxide). The adduct does not decompose under vacuum. In contrast to poly(sulphur oxide) it gets hydrolysed by water to form sulphite, sulphide, chloride and silica. Details of these investigations are given below.

EXPERIMENTAL

1. Preparation of poly(sulphur oxide). Dry sulphur (~20 g) and cupric oxide (~5 g) were well mixed using a pestle and mortar and filled into a reaction tube (Figure 1). The reactants were further dried by pumping under vacuum for 1 hour at room temperature. Previously weighed (empty) trap, T_1,

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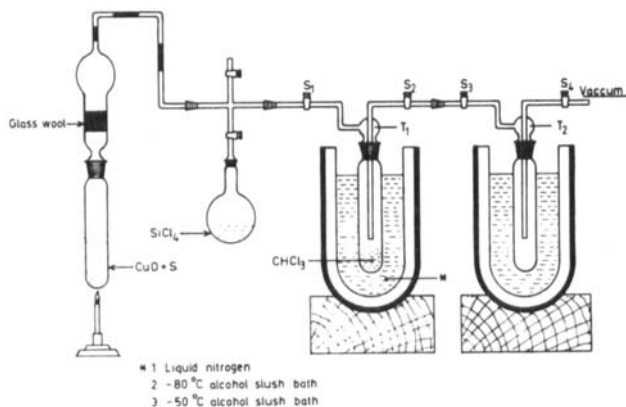† Author to whom all correspondence should be addressed.

FIGURE 1   Preparation of disulphur monoxide and the adduct.

containing 5 ml of dry chloroform and trap T_2, scavenger trap, were cooled by liquid nitrogen. The reactants were slowly heated in a flame till sulphur melted and then strongly heated (300–400°C) for about 15 minutes. Sulphur that sublimes deposits on the upper cooler parts of the reaction tube. The bottom of the tube was allowed to cool and then the condensed sulphur slightly warmed when it melted and fell over the copper oxide. Again the reactants were heated (300–400°C). This intermittent heating under vacuum was continued for 2 hours. The reaction tube was then allowed to cool. On attaining room temperature, stopcock S_1 was closed. The products collected in T_1, as multicoloured, pink, cherry red, yellow, blue, bluish green and brown solids. The first three colours in predominance. With the rotary pump running, the coolant liquid nitrogen under trap (T_1) was replaced by an alcohol slush bath a −80°C. Any gaseous product at this temperature from trap T_1 gets collected in trap T_2. After 2 hours at this temperature (in which time the solid appears deep yellow in colour), a slush bath coolant (−50°C) was introduced under T_1. T_1 was maintained at this temperature for about 2 hours and then allowed to attain room temperature by unattended natural warming up of the slush bath. The solid in trap T_1, appears bright yellow and is found to be very elastic. The pump was switched off after closing the stopcocks. Trap T_1, disconnected and the amount of product obtained was weighed. 300–400 mg of the compound was formed indicating a yield of about 2% only. The amount of sulphur dioxide, estimated iodometrically, collected in Trap T_2 was 850 mg indicating an overall yield of 5–6% based on the sulphur taken.

The yellow product in Trap T_1 was elastic and gave off a gaseous product slowly but continuously at room temperature. This yellow elastic solid was difficult to analyse for combined sulphur content so it was left aside for 3 to 4 days. After 4 days, it lost its elasticity and crumbled to a yellow powder. The IR spectrum of the solid was recorded on a Perkin Elmer model 599 spectrometer as a mull on KBr plates (Figure 2). The evolved gas from the elastic solid was identified as sulphur dioxide from its IR
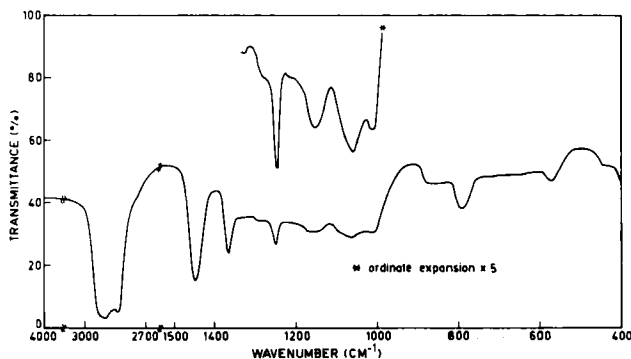
FIGURE 2   Infrared spectrum of poly(sulphur oxide).

TABLE I

Analysis of poly(sulphur oxide)

Sl. No.	Wt. of compound taken mg 1	Free(S) mg 2	Combined(S) mg 3	Total S (2+3) mg 4	% 'S'	Associated oxygen 1–4 mg 1–4	Moles(S) combined $\times 10^{-4}$	Moles (O) combined $\times 10^{-4}$	Ratio S/O	Formula
1	5.5	0.22	3.84	4.06	74	1.40	0.12	0.086	1.4	S_7O_5
2	7.6	2.29	3.89	6.18	81	1.42	0.122	0.089	1.4	S_7O_5
3	12.5	3.76	6.4	10.16	81	2.34	0.20	0.15	1.3	S_8O_6
4	15.8	0.75	01.84	11.59	73	4.21	0.34	0.26	1.3	S_8O_6

data. The yellow powdery solid was found to be insoluble in almost all organic solvents tried but softened in presence of benzene. The yellow solid was analysed for its sulphur content and found to have only 75–80% of sulphur (Table I). The rest in the yellow solid is assumed to be combined oxygen as this is the only gaseous reactant in the reaction and also the solid evolved SO_2 on thermal degradation. It is of interest to mention that the varied colours, yellow, pink, cherry red are known to be the colours exhibited by disulphur monoxide (S_2O) in condensed states and that S_2O decomposes to elemental sulphur and sulphur dioxide at room temperature.[2] Therefore, the yellow solid product should contain some free elemental sulphur along with combined sulphur in the form of its oxide. An elegant method, reduction with hydroiodic acid, developed in our laboratories can distinguish these two species.[3] A known weight of the compound was treated with hydroiodic acid (2 ml) and boiled, only combined sulphur gets reduced to hydrogen sulphide, while the elemental sulphur present alongside remains unattacked. The hydrogen sulphide formed was estimated. Results presented in Table I. The unattacked elemental sulphur floats in the solution. The iodine formed in the solution is treated with thiosulphate and the decolourised solution is treated with copper-powder (500 mg) along with 1 ml of benzene. The contents are refluxed for about 2 hours. Copper reacts with the elemental sulphur to form cuprous sulphide.[3] The contents on cooling, treating with hydroiodic acid and refluxing, evolves hydrogen sulphide which was estimated. (Table I). In a separate experiment, a known weight (10–20 mg) of the sample is treated with copper powder (500 mg) and the total sulphur content determined. It is known that combined[3] sulphur gets reduced by hydroiodic acid while elemental sulphur does not. But on addition of copper, elemental sulphur gets converted to Cu_2S and then this undergoes reduction by hydroiodic acid. Thus, reduction without addition of copper gives combined or associated sulphur and on treatment with copper, the total sulphur of the sample is accounted. The difference in weight between the weight of sample taken and the total sulphur content, gives the amount of oxygen associated with the combined sulphur. Results given in Table I.

2. Reaction of Poly(sulphur oxide) with Silicon Tetrachloride. An earlier reaction[5] has shown the formation of a gaseous adduct between sulphur monoxide and silicon tetrafluoride. Therefore, it was of interest to study the reaction of silicon tetrachloride with the lower oxide of sulphur. Preliminary studies indicated the formation of a solid adduct but this is admixed with poly(sulphur oxide) and therefore difficult to isolate and study. Therefore, an attempt has been made to understand the nature of the adduct as an admixture.

Procedure: The experimental set up is shown in Figure 1. Three modalities were tried (1) The disulphur monoxide (cherry red condensate at liquid nitrogen temperature) was prepared[1] and condensed into a trap containing 5 ml of dry chloroform. About 1 ml of silicon tetrachloride was condensed over this and then the contents were slowly thawed to room temperature. (2) The silicon tetrachloride (1 ml) was first condensed in Trap I and over this the disulphur monoxide was condensed. At the end of the experiment they were slowly thawed to room temperature and (3) The silicon tetrachloride vapour was admixed with the gaseous lower oxide of sulphur as it was passing into the condensing trap, Fig. 1 and simultaneously condensed. They were then thawed slowly to room temperature. Dry chloroform was taken to facilitate reaction. After 1 hour at room temperature, the chloroform and excess silicon tetrachloride were pumped off. The remaining poly(sulphur oxide) along with a part of silicon tetrachloride bound as an adduct was analysed. In all the three preparation modes, only a part of the excess silicon tetrachloride taken, formed an adduct and got imbedded along with the poly(sulphur oxide). Attempts to separate these two failed because none of the components sublimed in vacuum or had preferential nondestructive solvents. The solid adduct was studied as such.

RESULTS AND DISCUSSION

1. Poly(sulphur oxide)

From the results in Table I it is seen that approximately 50–65% of sulphur is retained as poly (sulphur oxide) and total sulphur is of the order of 75–82%. Therefore the ratio of combined sulphur to oxygen varies in the ratio 1:1.3 to 1.4 or the species is S_7O_5/S_8O_6 or both.

The IR spectra, (Figure 2), in nujol mull under ordinate expansion (as the solid is nearly insoluble in Nujol) shows absorption bands at $1250 \, cm^{-1}$, $1150 \, cm^{-1}$,

$1060\,cm^{-1}$, $1010\,cm^{-1}$, $780\,cm^{-1}$ and $560\,cm^{-1}$. These are assigned as follows based on earlier observations for sulphur-oxygen compounds.[4] The absorptions at $1250\,cm^{-1}$ and $1150\,cm^{-1}$ could correspond to symmetric S—O stretching vibrations and $1060\,cm^{-1}$ and $1010\,cm^{-1}$ to asymmetric stretching modes. The one at $780\,cm^{-1}$ could perhaps be assigned to $\nu_{(S-O-S)}$ and the absorption at $560\,cm^{-1}$ to $\nu_{S=S}$ stretching vibrations. The spectra thus indicates that all these modes are present in the powdery yellow solid. This solid is further found to thermally decompose to sulphur dioxide and sulphuroxide. Based on the above data it is suggested that the initally formed elastic linear polymer, poly(sulphur oxide) favours to undergo spontaneously with time cyclisation to a (S—O) bonded cyclic species with elimination of sulphur dioxide. This is further supported by the fact that cyclic sulphoxide exhibit stretching frequencies at $1050\,cm^{-1}$ and $1080\,cm^{-1}$ for the axial and equatorial S—O stretching frequencies.[4] For cyclic sulfites also these are observed[4] at $1190\,cm^{-1}$ and $1230\,cm^{-1}$. Since, the present species exhibits stretching vibrational modes, it is suggested that the elastic polymer, $1150\,cm^{-1}$ and $1250\,cm^{-1}$, cyclised to a ring structure and has a powdery nature similar to elemental sulphur. One of the several possible structures could be one similar to S_8 ring with a few alternate oxygens in the ring and a few coordinated to sulphur. In order to establish these properties to poly(sulphur oxide) only and not to unreacted sulphur, the sublimed sulphur from the reaction tube collected on the cooler parts of the reaction tube was heated separately in vacuum, no evolution of sulphur dioxide occurred. An IR spectrum of the solid sulphur in nujol was also recorded. It did not exhibit any absorption bands in the infrared region. These indicate that the sublimed sulphur has not formed the poly(sulphur oxide), only the poly(sulphur oxide) species has been formed during the thawing of the condensate held at liquid nitrogen temperature to room temperature. The freshly formed elastic yellow solid is a linear polymer as has been reported earlier.[7,8] However, this with time (3 to 4 days) rearranges itself to a powdery cyclic sulphur oxide (with the elimination of sulphur oxide) and has a cyclic structure similar to elemental sulphur. The sulphur dioxide has been characterised by its IR spectrum.

2. Adduct of lower oxide of sulphur with silicon tetrachloride

An interesting feature of the solid adduct was that it decomposed in presence of water to sulphite, sulphide, chloride and silica whereas the poly(sulphur oxide) was unaffected by water at room temperature. Only on boiling or treatment with alkali, poly(sulphur oxide) undergoes slow hydrolysis. Results of the hydrolyses of the adduct given in Table II indicate that the adduct could be $S_2O\cdot SiCl_4$, a pentacoordinated with respect to silicon or $(SO)_2SiCl_4$, hexacoordinated with respect to silicon. IR data supports hexacoordinated silicon.

After hydrolysis the remaining solid was dried and analysed. The IR analysis of the dry solid (Fig. 3) shows two characteristic absorption peaks of silica, a strong broad band between, $1100-1000\,cm^{-1}$ and a medium intensity bond at $480\,cm^{-1}$. This indicates that the adduct is not associated with the poly(sulphur oxide) but only coexists as it forms silica as one of the products of hydrolysis. Thus, silicon is

TABLE II

Analysis of the adduct $SiCl_4(SO)_2$

(Total volume of the hydrolyzed solution = 250 ml)

	Cl* mg	S* mg	S2O† mg	SO† mg	SO† moles × 10⁻⁴	S2O† moles × 10⁻⁴	SiCl4† mg	SiCl4† moles × 10⁻⁴	Ratio Moles SO/SiCl4	Ratio Moles S2O/SiCl4
1.	10.77	4.47	5.89	6.70	0.140	0.070	12.90	0.076	1.84	0.92
2.	4.72	2.23	2.80	3.35	0.070	0.035	5.65	0.033	2.12	1.06
3.	7.55	3.57	4.50	5.40	0.113	0.056	9.04	0.053	2.13	1.06

* Experimentally determined values.

† Calculated values from the determined values for sulphur, oxygen and chlorine.

TABLE III

Analysis of poly(sulphur oxide) containing the adduct of silicon tetrachloride

Sl. No.	Wt. of sample taken mg 1	S without Cu 'CS' mg 2	% CS 3	S with Cu mg 4	% 'S' 5	Difference 'S' associated with adduct [2-4]	% 'S' associated with adduct	'O' associated mg	Moles 'O' × 10⁻⁴	Moles 'CS' × 10⁻⁴	Ratio* S:O	Formula of (SO)x
1.	19.5	15.26	80	—	—	—	—	4.24	0.265	0.477	1,8	S_9O_5
2.	14.9	11.66	78	11.20	75	0.46	3	3.24	0.203	0.364	1,8	S_9O_5
3.	10.3	8.36	81	7.91	77	0.45	4	1.94	0.121	0.26	2.2	$S_{11}O_5$

CS: combined sulphur.

* This is on assumption that all sulphur is associated and amount of free sulphur is less than 1 mg seen from Table I
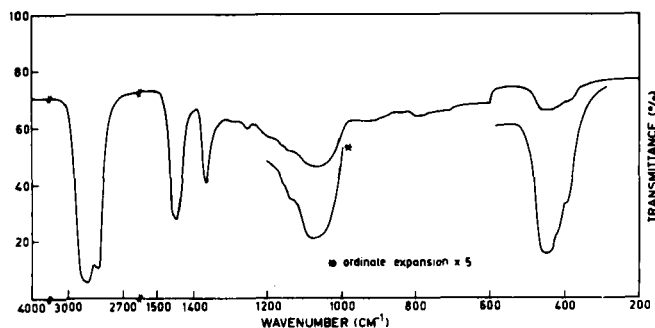
FIGURE 3   Infrared spectrum of the hydrolysed residue (dried)–silica.

not associated in the (S—O) chain or ring but is an independent adduct species. Secondly, on treatment with copper, the adduct coordinates with copper and stabilizes the sulphur of the sulphur species (SO) attached to silicon such that it does not undergo reduction by hydroiodic acid. Normally combined sulphur can be reduced by hot hydroiodic acid. The reduction of the adduct without the addition of copper gives the amount of combined sulphur present, whereas, addition of copper stabilizes the adduct against hydrogen iodide cleavage. Thus, from the results of poly(sulphur oxide) containing the adduct, Table III, it is observed that the amount of reducible sulphur (combined sulphur) is greater than that after treatment with copper indicating that hydroiodic acid is unable to cleave the bond, silicon-sulphur, as it gets attached to copper making it irreducible by hydroiodic acid. Thus, this copper attached sulphur is the amount of sulphur that combines with silicon tetrachloride as the adduct. This amount is only 1/10th of the available sulphur in poly(sulphur oxide). These results indicate that silicon tetrachloride though present in excess does not react with all the available species of sulphur but only with one type perhaps only with [SO] as in the case of silicon tetrafluoride.[5] It is well known[2] that SO has a short life time, momentarily stable in gas phase; dimerising and then undergoing three body collision to give SO_2 and elemental sulphur. The adduct results before such decomposition occurs.
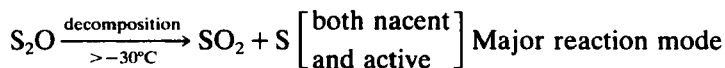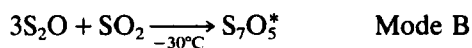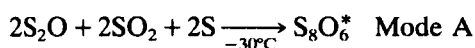
The IR spectrum (Figure 4) of the imbedded adduct in poly(sulphur oxide) as a
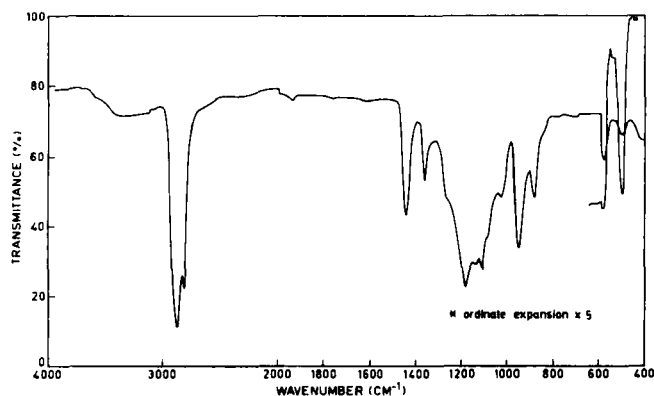
FIGURE 4   Infrared spectrum of the adduct $(SO)_2$ $SiCl_4$.

mull, indicates the following absorption bands. 1195 cm^{-1}, 1140 cm^{-1}, 1110 cm^{-1}, 1020 cm^{-1}, 950 cm^{-1}, 880 cm^{-1}, 580 cm^{-1}, 500 cm^{-1}. Though a complete assignment is not attempted, it is sufficiently clear that the ν_{Si-Cl} in SiCl$_4$ at 620 cm^{-1} has moved to 580 cm^{-1} and/or 500 cm^{-1} indicative of the presence of 2 ligands L$_2$SiCl$_4$ in cis configuration and the vibrations at 950 cm^{-1} and 880 cm^{-1} could perhaps be due to ν_{Si-O-S}. The other vibrations correspond to S—O frequencies. Another interpretation for the absorptions at 580 cm^{-1} and 500 cm^{-1} could be as follows. The 580 cm^{-1} corresponds to the ν_{Si-Cl} and the one at 500 cm^{-1} corresponding to ν_{Si-S}. This then corresponds to an adduct with a pentacoordinate silicon attached to sulphur. S$_2$O·SiCl$_4$. The analysis of the water hydrolysed adduct (Table III) is unable to distinguish with certainty. Since hexacoordinated species are more stable with SiCl$_4$ it is suggested that the adduct formed is (SO)$_2$SiCl$_4$ or L$_2$SiCl$_4$ in cis configuration based on earlier reports for ν_{Si-Cl}. Experiments indicate that copper coordinates with the bound sulphur of the adduct and stabilizes the S=O and Si—S bond towards cleavage by hydroiodic acid. The amount of sulphur associated with the adduct (Table III) is of the order of 3–5 mg, the amount of poly(sulphur oxide) formed is around 300 mg indicating that only 1% reacts with SiCl$_4$. Two reasons can account for this low yield, as the SiCl$_4$ taken is in excess. One, the species that coordinates is transiently formed at a low temperature for which we have no control (SO has a half life of 2–5 m sec at 20°C and 0.001 t) or the tendency to form poly(sulphur oxide) is competitive in relation to reaction with silicon tetrachloride. It is of interest to mention that in a separate experiment it has been found that sulphur dioxide does not react with silicon tetrachloride.

Based on the above arguments the reaction mode could be formulated as follows:

A. *Poly(sulphur oxide)*

$$2S_2O + 2SO_2 + 2S \xrightarrow[-30°C]{} S_8O_6^* \quad \text{Mode A}$$

$$3S_2O + SO_2 \xrightarrow[-30°C]{} S_7O_5^* \qquad \text{Mode B}$$

$$S_2O \xrightarrow[>-30°C]{\text{decomposition}} SO_2 + S \begin{bmatrix} \text{both nacent} \\ \text{and active} \end{bmatrix} \text{Major reaction mode}$$

A figurative representation of the bent structures of these molecules with discrete unit similar to crown structure of sulphur along with cross bridging of sulphur with oxygen could be envisaged as follows:
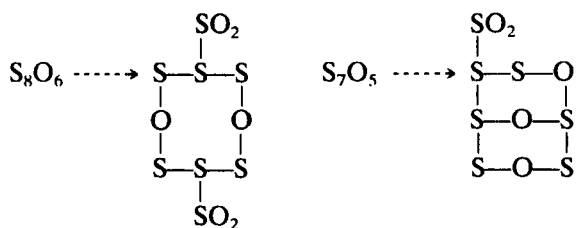
Experimentally i.e. by analysis, it has been observed in the present investigation that a small percentage of the S—O—S bond is very stable and does not cleave even at 100°C in vacuum though the solid melts and a small percentage of SO_2 is released. On cooling the solid still possesses S—O—S linkage. The held SO_2 on the other hand is found to be labile and cleaves easily on warming and has been identified spectroscopically.

It is interesting to note the following:

(a) S_8O_6 or S_7O_5 do not react with $SiCl_4$ at the experimental conditions i.e. up to room temperature. However, reaction occurs with an intermediate species (SO) produced during the decomposition of S_2O at $-30°C$, alternatively S_2O itself could react just before decomposing

$$SiCl_4 + S_2O \rightarrow SiCl_4 \cdot S_2O \qquad (i)$$

$$SiCl_4 + 2[SO] \rightarrow SiCl_4 \cdot 2[SO] \qquad (ii)$$
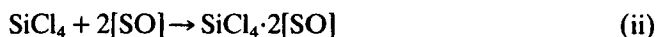
The IR data indicates silicon is hexacoordinated and therefore (ii) is the predominant species. The low yield of the adduct indicates that the predominant reaction is the decomposition S_2O to the linear polymer $[S_2O]_x$ which cyclices to a cyclic polymer S_8O_6 and S_7O_5 (mode A). A small percentage (2%) of (SO) however reacts with $SiCl_4$ forming the adduct $SiCl_4 \cdot 2(SO)$ which gets imbedded in the solid polymers.

(b) The adduct is a distinct product from the cyclo [polysulphur-oxide] S_8O_6 or S_7O_5, as it undergoes hydrolysis whereas S_8O_6/S_7O_5 does not, even with dilute alkali [0.1 N]. The adduct has been formulated as $SiCl_4 \cdot 2[SO]$.

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