

Sulfur/carbon double and triple bonds

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Abstract - Preparation and structural behaviour of the three classes of sulfur compounds $R_2C=SF_4$, $R-C\equiv SF_3$ and $R_2C=SOF_2$ is described. The alkyldiene sulfur tetrafluorides are formed by elimination of $C-SF_5$ compounds or by special isomerization reactions. They exhibit a rigid trigonal bipyramidal structure with the double bonded carbon in the equatorial position, and the carbon substituents in the axial plane.

The alkyldiyne sulfur trifluorides are analogous to acetylenes, however they are not completely linear, although the extent of this is still disputed.

The alkyldiene sulfur difluoride oxides are formed by hydrolysis of the corresponding sulfur tetrafluorides. They show a complicated non rigid behaviour.

INTRODUCTION

In main group chemistry of the last few years many successful preparations of multiple (mainly double) bonds between heavier elements have been achieved. Phosphorous and silicon have been most in focus in these investigations, and the double bonds are generally stabilized by steric crowding which prevents coordinative saturation of such bonds.

Here we present results which show that sulfur is a particularly good candidate for multiple bonding, even in the absence of steric crowding.

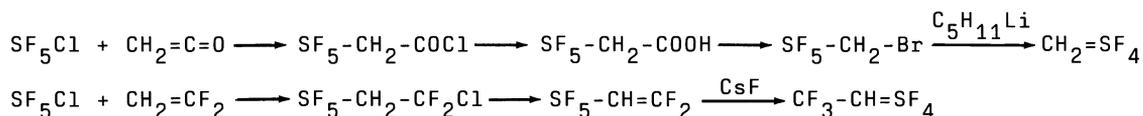
Multiple bonds between sulfur and oxygen or nitrogen are commonly known (SO_2 , NSF_3), but these bonds are expected to have a strong polar character, with less electronegative elements, e.g. carbon, quite non polar multiple bonds are expected. Thioketones and sulfenes are often quite instable or reactive, respectively. The only real exception seems to be CS_2 .

Fluorine substitution has been shown to be very helpful in stabilizing multiple bonds between sulfur and carbon. It

- a) increases the coordination of sulfur, preventing dimerization and polymerization reactions
- b) increases the electronegativity of the sulfur thus minimizing bond, polarization towards carbon
- c) decreases the size of sulfur orbitals thus providing better π overlap with carbon orbitals.

ALKYLIDENE SULFUR TETRAFLUORIDES

Table 1 shows the $R_2C=SF_4$ molecules known so far. The preparation of these compounds requires in all cases the generation of a $C-SF_5$ containing precursor, followed by HX elimination and/or a fluoride migration process:



Quite often the main problem is the generation of suitable starting materials. The alkylidene sulfur tetrafluorides are low boiling, colourless liquids (or gases) which are surprisingly stable. Electron withdrawing groups on carbon further increase thermal stability, possibly by preventing carbene formation:



The structure can in all cases be derived from a rigid trigonal bipyramid (ref. 6,7,8), see Fig. 1.

TABLE 1. Alkylidene sulfur tetrafluorides

Compound	bp	method of preparation
$CH_2=SF_4$ ¹	-19	$Br-CH-SF_5 + C_5H_{11}Li$
$CH_3-CH=SF_4$ ²	+27	$CH_3-CHBr-SF_5 + C_4H_9Li$
$CF_3-CH=SF_4$ ^{3,4}	+17	Isomerization of $CF_2=CH-SF_5$ or $CF_3-CHBr-SF_5 + C_4H_9Li$
$CF_3(CH_3)C=SF_4$ ³	+41	$CF_3(CH_3)CBr-SF_5 + C_4H_9Li$
$COF-CH=SF_4$ ⁵	~70	Isomerization of $O=C-CH-SF_5$

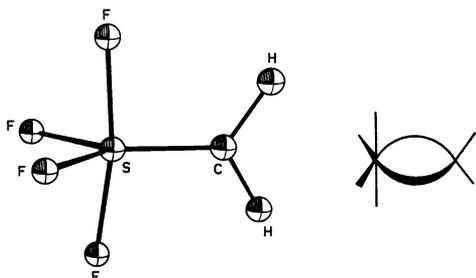


Fig. 1. Structure of $CH_2=SF_4$ according to crystal structure, electron diffraction and ab initio calculations, and a simplified interpretation explaining axial positions of the carbon substituents and the non-rigidity.

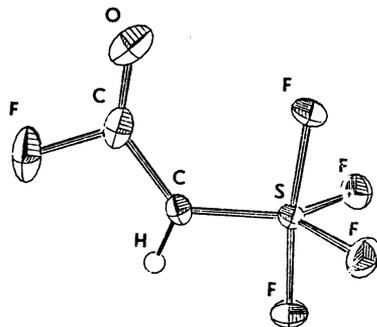


Fig. 2. Crystal structure of $COF-CH=SF_4$: All atoms except the equatorial fluorine atoms lie on a mirror plane. CS and CO double bonds are conjugated in a cisoid fashion.

The non-rigidity of the $R_2C=SF_4$ compounds can easily be established by nmr methods: axial and equatorial fluorine atoms on sulfur are chemically and magnetically non equivalent and do not interchange upon heating till $100^\circ C$. Thus very complicated spectra are observed which can only be interpreted by computer simulation (ref. 2,3,5,9). The rigidity of these five coordinate sulfur compounds (c.f. SOF_4 is non rigid even at $-160^\circ C$) is explained by the strength and orientation of the CS double bond which keeps the fluorine atoms in place.

The structure of $COF-CH=SF_4$ presents a special case, since the CO double bond is conjugated to the CS double bond. X-ray structural analysis as shown in Fig. 2 reveals the overall planarity of the entire molecule, except for the equatorial fluorine atoms. The CS bond is lengthened a little (160.3 pm), the CC bond is very short (146.1 pm), so that it can be compared with butadiene. But surprisingly, the CO and CS double bonds are fixed in a cisoid position.

The chemistry of the alkylidene sulfur tetrafluorides, so far as it is known, consists mostly of addition across the double bond. The direction of addition indicates that here is a (small) ylidic character to the double bond, sulfur carrying the positive charge.



ALKYLIDYNE SULFUR TRIFLUORIDES

Thus far further HF elimination leading to a triple bond could only be achieved (9) in a single case: $CF_3-CH=SF_4 \longrightarrow CF_3-C\equiv SF_3 + HF$

This triple bonded material is colourless, b.p. 5° ; it is unstable.

Its structure is seen in Fig. 3 (ref. 10).

The CS bond length is the shortest known so far. The non-linearity of this heteroacetylenic system has created some dispute. The CCS angle found by x-ray is 171.5° ; however electron diffraction indicates an angle of about 155° . *Ab initio* calculations with increasing sophistication resulted in bond angles of 180° (ref. 11), 171.5° (ref. 12), and $140-150^\circ$ (ref. 13).

This serious discrepancy can tentatively be explained as follows: The potential surface as a function of CCS angle-bending is extremely flat. To locate a minimum is very difficult. The preliminary summary of all the data is that the molecule is bent under all circumstances. The small deviation from linearity in the crystal may be a result of lattice forces which straighten the inherently more bent molecule.

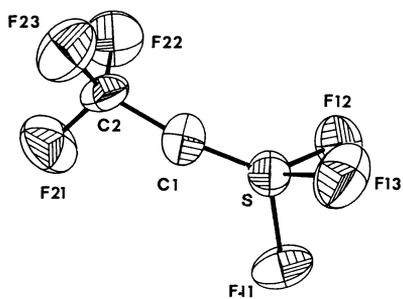
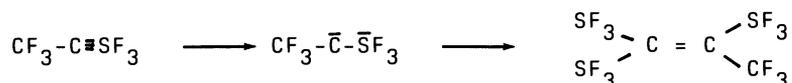


Fig. 3. Crystal structure of $CF_3-C\equiv SF_3$. Note the very short CS bond length, the bond angles of almost 90° between the sulfur fluorine atoms and, above all, the non-linearity of the $C-C\equiv S$ array.

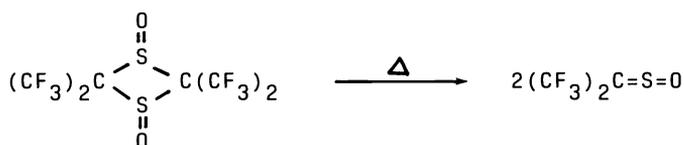
The chemistry of $\text{CF}_3\text{C}\equiv\text{SF}_3$ is restricted due to its limited stability. HF was successfully added. Upon decomposition it dimerizes:



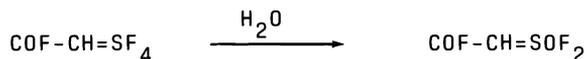
For this dimerization reaction a carbene mechanism is proposed.

ALKYLIDENE SULFUR DIFLUORIDE OXIDES

The influence of oxygen atoms bonded to certain elements is often similar to that of fluorine. In 1985 a stable sulfene was generated by four membered ring cleavage (ref. 14).

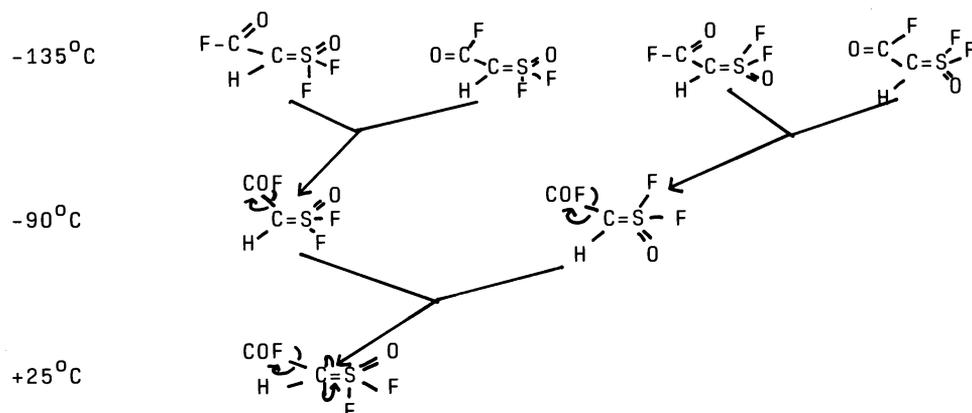


Simple hydrolysis of a specific alkylidene sulfurtetrafluoride resulted in fluorocarbonylmethylene sulfur difluoride oxide:



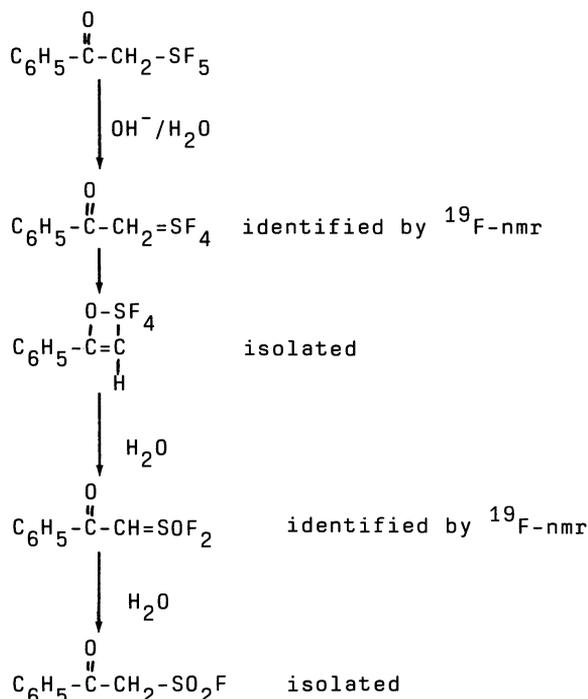
This reaction is so far not transferable to the other $\text{R}_2\text{C}=\text{SF}_4$ materials, and is probably more complex than it looks, see below.

This novel material presents a very complicated non rigid structural problem. There are two possible orientations of the SO groups relative to the COF group, namely cis and trans, and furthermore the CO double bond can be oriented toward the CS double bond in cisoid or transoid conformation, fixed by conjugation. Three of the four isomers are observed at -135°C . COF rotation interchanges two of them at -90°C , and at room temperature torsion of the CS double bond interchanges all isomers.



These findings have been verified by ^{19}F and ^1H nmr spectroscopy.

The hydrolysis reaction mentioned above is not so simple as may be assumed. In another case a whole array of compounds has been identified by nmr methods, although only one intermediate and the final product have been isolated.



BOND CHARACTERISTICS

A comparison of bond lengths, force constants and bond energies shows that these bonds are indeed multiple bonds.

TABLE 2. Bond characteristics of single, double and triple bonds

Compound	force constant n/m	bond energy kJ/mol	bond length pm
$\text{H}_3\text{C}-\text{CH}_3$	450	347	154.2
$\text{H}_2\text{C}=\text{CH}_2$	980	611	133.7
$\text{HC}\equiv\text{CH}$	1560	837	120.3
$\text{H}_3\text{C}-\text{SO}_2\text{F}$	304	255 a)	175.9
$\text{H}_2\text{C}=\text{SF}_4$	633	377	155.3
$\text{CF}_3\text{C}\equiv\text{SF}_3$	1253	?	142.0

a. value for R_2S

The force constants in CC single, double and triple bonds are approximately 1:2:3, of the corresponding CS bonds 1:2:4. The bond length of the double bonds are in both cases about 13% shorter than the single bonds, the triple bonds are again 9% shorter than the double bonds for both systems.

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- $$\text{CF}_5\text{-CH=SF}_4 \xrightarrow{\text{KOH}} \text{CF}_3\text{-C}\equiv\text{SF}_3$$
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