Journal of Fluorine Chemistry, 60 (1993) 85–91

Single electron transfer catalyzed simultaneous cleavage of C–S and S–S bonds

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(Received December 18, 1991; accepted March 23, 1992)

Abstract

Since the S–S bond of polysulfides plays a vital role in biological processes, the chemistry of the S–S bond has attracted considerable attention. The reaction of bis-(trifluoromethyl) trisulfide with organolithium reagents at − 78 °C has now been found to cause simultaneous scissions of the C–S and S–S bonds and to furnish mixed monosulfides, disulfides and trisulfides containing the trifluoromethyl moiety. The formation of the various products has been rationalized on the basis of the involvement of the single electron transfer process.

Ubiquitously occurring disulfides and trisulfides [1] have attracted considerable attention because of their contribution to the tertiary structure of the proteins [2], involvement in energy transfers [3] and industrial applications [4]. The importance and usefulness of these compounds primarily rests on the presence and reactivity of the S–S bond. Its reactions with nucleophiles and electrophiles are numerous and take place heterolytically [5]. Homolytic cleavage [6] can be effected under photolytic [7], thermal [8], electrolytic [9] or radiolytic [9] conditions. The scission generally occurs at the S–S bond [6h, 10a], for the C–S bond of the disulfide is 5–10 kcal mol^{-1} stronger than the S–S bond [10b–e]. It must be stated that two exceptions to this generalization are known, in that the scission of the C–S bond is favored in these cases, for the free radicals thus generated are more stable than the free radicals formed by the S–S bond cleavage [10f, g]. The nature and the mechanism of the cleavage of C–S and S–S bonds of bis-(trifluoromethyl) trisulfide by organolithium reagents are described in this paper.

In contrast with the disulfides, the S–S bond of the tetrasulfides appears to undergo thermolysis readily [11a, b]. Flash photolysis of butyl tetrasulfide is known to produce perthiyl radicals [11b]. This has led to the conclusion that polysulfide radicals $R\dot{S}_n$ ($n \geqslant 2$) are considerably more stable than thiyl radicals [11c]. This inference has been further substantiated by molecular orbital calculations [11d], by the chemical unreactivity of the perthiyl radicals

[11c] and by the concept of a three-electron bond between the terminal sulfur atoms [11e].

Surprisingly, there has been no definitive study of the S–S bond scission of the trisulfides [12a–c]. In principle, the homolysis of the S–S bond of the trisulfides should be more facile than that of the disulfides, furnishing both thiyl and perthiyl radicals. This assumption is indirectly supported by the observation that photolysis of dimethyl trisulfide yielded disulfides, trisulfides and tetrasulfides by the fission of the S–S bond [12d] and by the relatively low yields of the mixed trisulfides (see Table 1). Since the activation energy for the trisulfide exchange between ethyl and n-propyl trisulfides was found to be only 29 kcal mol^{-1} and produced only a single product, namely ethyl n-propyl trisulfide, the involvement of a free-radical chain reaction and the attack on the central sulfur have been postulated [12e]. However, this suggestion is inconsistent with the observation that the central sulfur atom remained unchanged during exchange reactions conducted with substrates in which the central sulfur atom was labeled [12f]. Also, photolysis of a trisulfide has been reported to give a mixture of disulfides, trisulfides and tetrasulfides [12d]. As a result of this apparent contradiction, the mechanism of the S–S bond scission of the trisulfides remains as yet undefined [12f].

Recently an improved synthesis of bis-(trifluoromethyl) trisulfide (**1**) has been described [13a]. Organolithium reagents in the past have been shown to cleave the S–S bond [13b–f]. It was considered that the reaction of **1** with organolithium compounds, which have been known to react with various substrates via a single electron transfer (SET) process [14] may shed some light on the cleavage of the S–S bond by free radicals generated through the SET process. This expectation was supported by the fact that the highly electronegative CF_3 group was expected to weaken the S–S bond.

The results of the reaction of **1** with various organolithium reagents (RLi) at − 78 °C are summarized in Table 1. Thus CF_3SSSR, CF_3SSR, CF_3SR, RSSR and RSR were obtained. Only C_6H_5Li failed to give the asymmetrical

TABLE 1

Distribution of products formed from the reaction of bis-(trifluoromethyl) trisulfide with organolithium reagents[a]

$CF_3SSSCF_3 + RLi \longrightarrow CF_3SSSR + CF_3SSR + CF_3SR + RSSR + RSR + R–R$

R	CSF_2	CF_3SSSR	CF_3SSR	CF_3SR	RSSR	RSR	R–R
CH_3		0.5%	6.3%		0.7%		
n-C_4H_9	0.1%	3.5%	15.5%	7.3%	3.9%	48.4%	8.1%
s-C_4H_9		1.9%	4.2%		0.7%	4.5%	
t-C_4H_9		28.0%	35.0%		17.0%	11.0%	
Me_3SiCH_2[b]		3.4%	21.3%	1.4%			2.1%
C_6H_5			7.1%	10.1%			10.4%

[a] Similar results have been obtained with lithium diisopropylamide (LDA).

[b] $(CH_3)_3SiC(S)SCF_3$ has also been identified as a byproduct of this reaction.

trisulfide. The yields of the hydrocarbons formed from the dimerization of the alkyl radicals derived from the organolithium reagents are comparable with those arising from photolysis [12a, b]. Thiocarbonyl fluoride (**3**) (Table 1) identified as a byproduct may have originated from either F_3CS or F_3CSH. The latter was not characterized as such but is known to give rise to **3** in aqueous media [12c].

The formation of the products described in Table 1 can be rationalized on the basis of the homolysis of both the C–S and the S–S bonds initiated by the SET mechanism (Scheme 1). Since sulfur atoms are highly susceptible to radical attack, the S–S bond should be quite reactive towards free radicals. Free-radical propagation begins with the transfer of an electron from the organolithium reagent to **1** and the fragmentation of the initially formed radical anion–radical cation pair which collapses to give a sulfuryl radical and the trifluoromethyl anion [13f]. All the products predicted and expected from the SET process have been characterized with the exception of the alkyl trisulfide (step (6)).

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\begin{array}{lcl}
\mathrm{CF_3SSSCF_3 + RLi} & \longrightarrow & \mathrm{[(CF_3SSSCF_3)^{\dot{-}} + \dot{R} + Li^+]} \\
\mathrm{(CF_3SSSCF_3)^{\dot{-}}} & \longrightarrow & \mathrm{CF_3SS\dot{S} + \bar{C}F_3} \\
\mathrm{CF_3SS\dot{S} + \dot{R}} & \longrightarrow & \mathrm{CF_3SSSR} \\
\mathrm{CF_3SSSR + RLi} & \longrightarrow & \mathrm{[(CF_3SSSR)^{\dot{-}} + \dot{R} + Li^+]} \\
\mathrm{(CF_3SSSR)^{\dot{-}}} & \longrightarrow & \mathrm{RSS\dot{S} + \bar{C}F_3} \\
\mathrm{RSS\dot{S} + \dot{R}} & \longrightarrow & \mathrm{RSSSR} \\
\mathrm{(CF_3SSSCF_3)^{\dot{-}}} & \longrightarrow & \mathrm{CF_3S\dot{S} + \bar{S}CF_3} \\
\mathrm{CF_3S\dot{S} + \dot{R}} & \longrightarrow & \mathrm{CF_3SSR} \\
\mathrm{CF_3SSR + RLi} & \longrightarrow & \mathrm{[(CF_3SSR)^{\dot{-}} + \dot{R} + Li^+]} \\
\mathrm{(CF_3SSR)^{\dot{-}}} & \longrightarrow & \mathrm{CF_3\dot{S} + R\bar{S}} \\
\mathrm{CF_3\dot{S} + \dot{R}} & \longrightarrow & \mathrm{RSCF_3} \\
\mathrm{(RSSCF_3)^{\dot{-}} + CF_3SSSCF_3} & \longrightarrow & \mathrm{RSSCF_3 + (CF_3SSSCF_3)^{\dot{-}}} \\
\mathrm{(RSSCF_3)^{\dot{-}}} & \longrightarrow & \mathrm{RS\dot{S} + \bar{C}F_3} \\
\mathrm{RS\dot{S} + \dot{R}} & \longrightarrow & \mathrm{RSSR} \\
\mathrm{(RSSCF_3)^{\dot{-}}} & \longrightarrow & \mathrm{R\dot{S} + \bar{S}CF_3} \\
\mathrm{R\dot{S} + \dot{R}} & \longrightarrow & \mathrm{RSR} \\
\mathrm{2\dot{R}} & \longrightarrow & \mathrm{R\text{-}R} \\
\mathrm{Li^+ + \bar{C}F_3} & \longrightarrow & \mathrm{[LiCF_3] \longrightarrow polymer}
\end{array}
$$

Scheme 1.

Dismutation of the C–S bond during photolysis has precedents [12d]. Trifluoromethyllithium (step (18)) has been stated to form an unknown polymer [13f]. The proposed scheme derives its strength and support from the following.

(1) Many substitution reactions on sulfur have been suggested to occur via a cascade of addition–eliminations rather than through a one-step displacement [6f].

(2) There are precedents for thiaphilic addition and electron sharing by radicals and nucleophiles with sulfur singly bonded to carbon [5d, 14a].

(3) A similar mechanism has been made to explain the unusual reactivity of bis-(trifluoromethyl) disulfide with organolithium reagents [14b].

(4) The SET pathway has been suggested as the preferred course even in the case of sterically hindered systems [14c–e].

(5) The formation of thiyl, perthiyl and sulfuranyl radicals has been invoked to rationalize the products formed from the thermolysis of the trisulfides [12e].

(6) The formation of the dimerized hydrocarbons is generally regarded as proof of the involvement of free radicals.

(7) The presence of the electronegative CF_3 group in the molecule must definitely weaken both C–S and S–S bonds and thus render them more reactive towards free radical reactions.

Experimental details

Warning! Because of the high toxicity associated with bis-(trifluoromethyl) trisulfide, efficient hoods and extreme care should be used in working with this compound. All solvents were dry and freshly distilled prior to their use. The reactions were carried out in a flame-dried argon-gas-purged 10 or 25 ml three-necked flask equipped with a magnetic stirrer, a gas inlet, a pressure-equalizing dropping funnel and a reflux condenser carrying a Dry Ice–acetone trap. The temperature of the coolant passing through the condenser was maintained at −20 °C. All reactions were carried out by adding the alkyllithium reagent (0.01 mol) to the trisulfide (0.01 mol) cooled to −78 °C. The reactions were terminated by the addition of moist ether and aqueous ammonium chloride, followed by extraction with ether. After drying over sodium sulfate, the solvent was evaporated under reduced pressure and the residue flash distilled and analyzed by gas chromatography (GC)–mass spectroscopy. Mass spectra were obtained on a Finnigan Model 5100 gas chromatography–mass spectrometer equipped with a silica SE-54 capillary column 25 m long and 0.31 mm inside diameter (J and W Scientific, Rancho Cordova, CA). Routine GC analyses were accomplished with a Hewlett–Packard 5890A gas chromatograph equipped with a J and W Scientific DB-5 column 30 m long and 0.53 mm inside diameter (J and W Scientific, Folsom, CA). Table 2 gives the mass spectral fragmentation data of compounds formed during the reaction of bis-(trifluoromethyl) trisulfide with organolithium reagents at −78 °C.

Molecular ion peaks are observed for all compounds except two. The splitting off of SCF_3 ($m/e = 101$) and CF_3 ($m/e = 69$) appears to be a common characteristic of compounds containing the SCF_3 moiety. In the case of mixed sulfides containing trifluoromethyl and alkyl groups, the ion corresponding to CSH ($m/e = 45$) is commonly observed. In the reaction of *n*-BuLi with **1**, octane (retention time, 3.12 min) was characterized as one of the products. This evidently resulted from the dimerization of the butyl radical, which is formed from the organolithium reagent itself. The formation of the dimerized product(s) is regarded as definite proof of the involvement of a free radical process. Also, the origin of t-butyl pentyl sulfide formed

TABLE 2

Mass spectral fragmentation of monosulfides, disulfides, trisulfides and dimerized products formed during the reaction of bis-(trifluoromethyl) trisulfide with organolithium reagents

CH_3SSCF_3 (retention time, 0.38 min)	$M^+ = 148$; 129 (M–F); 101 (SCF_3); 82 (CSF_2); 79 (M–CF_3, 100%); 63 (CSF); 50 (CF_2); 45 (CSH)
CH_3SSSCF_3 (retention time, 2.24 min)	M^+ (not seen); 133 (M–SCH_3); 82 (CSF_2); 69 (CF_3, 100%); 64 (SS); 45 (CSH)
CH_3SSCH_3 (retention time, 0.33 min)	$M^+ = 94$ (100%); 79 (M–CH_3); 65 (SSH); 64 (SS); 60 (M–H_2S); 47 (SCH_3)
n-$C_4H_9SCF_3$ (retention time, 2.18 min)	$M^+ = 158$; 129 (M–C_2H_5); 115 (M–C_3H_7); 89 (M–CF_3); 82 (CSF_2); 69 (CF_3); 63 (CSF); 59 (SC_2H_3); 57 (C_4H_9); 56 (C_4H_8, 100%); 45 (CSH)
n-$C_4H_9SSCF_3$ (retention time, 3.43 min)	$M^+ = 190$; 171 (M–F); 161 (M–C_2H_5); 147 (M–C_3H_7); 133 (CF_3SS); 101 (SCF_3); 82 (CSF_2); 69 (CF_3); 64 (SS); 57 (C_4H_9, 100%); 45 (CSH)
n-$C_4H_9SSSCF_3$ (retention time, 6.07 min)	$M^+ = 222$; 165 (M–C_4H_9); 133 (CF_3SS); 101 (SCF_3); 87 (C_4H_7S); 64 (SS); 57 (C_4H_9, 100%); 45 (CSH)
n-$C_4H_9SSC_4H_9$ (retention time, 9.23 min)	$M^+ = 178$; 122 (M–C_4H_8); 87 (C_4H_7S); 79 (122-C_3H_7); 64 (SS); 57 (C_4H_9, 100%); 45 (CSH)
n-$C_4H_9SC_4H_9$ (retention time, 6.22 min)	$M^+ = 146$; 117 (M–C_2H_5); 103 (M–C_3H_7); 90 (M–C_4H_8); 75 (90-CH_3); 61 (SC_2H_5, 100%); 56 (C_4H_8); 47 (SCH_3); 45 (CSH)
CSF_2 (retention time, 1.12 min)	$M^+ = 82$ (100%); 63 (CSF); 51 (SF); 50 (SF_2)
Bu^sSSSCF_3 (retention time, 3.33 min)	$M^+ = 222$; 157 (M-65); 89 (M–CF_3SS); 57 (C_4H_9, 100%); 45 (CSH)
Bu^sSSCF_3 (retention time, 2.20 min)	$M^+ = 190$; 161 (M–C_2H_5); 147 (M–C_3H_7); 101 (SCF_3, 100%); 57 (C_4H_9); 45 (CSH)
Bu^sSSBu-s (retention time, 5.14 min)	$M^+ = 178$; 122 (M–C_4H_8); 87 (SC_4H_7); 66 (H_2S_2); 57 (C_4H_9, 100%); 45 (CSH)
Bu^sSBu-s (retention time, 3.12 min)	$M^+ = 146$; 131 (M–CH_3); 117 (M–C_2H_5); 89 (M–C_4H_9); 75 (117-C_3H_6); 61 (C_2H_5S, 100%); 57 (C_4H_9); 45 (CSH)
Bu^tSSSCF_3 (retention time, 4.46 min)	$M^+ = 222$; 207 (M–CH_3); 165 (M–C_4H_9); 133 ($SSCF_3$); 121 (C_4H_9SS); 96 (SSS); 82 (CSF_2); 69 (CF_3); 64 (SS); 57 (C_4H_9, 100%); 45 (CSH); 41 (C_3H_5)
Bu^tSSCF_3 (retention time, 2.51 min)	$M^+ = 190$; 171 (M–F); 133 (CF_3SS); 101 (CF_3S); 73 (SC_3H_5); 69 (CF_3); 64 (SS); 57 (C_4H_9, 100%); 45 (CSH); 41 (C_3H_5)
Bu^tSSBu-t (retention time, 6.38 min)	$M^+ = 178$; 122 (M–C_4H_8); 107 (122-CH_3); 89 (SC_4H_9); 69 (CF_3); 64 (SS); 57 (C_4H_9); 45 (CSH); 41 (C_3H_5, 100%)
Bu^tSBu-t (retention time, 3.56 min)	$M^+ = 146$; 131 (M–CH_3); 90 (C_4H_9SH); 75 (C_3H_6SH); 57 (C_4H_9, 100%); 45 (CSH); 41 (C_3H_5)
$Bu^tSC_5H_{11}$ (retention time, 8.22 min)	$M^+ = 192$; 136 (M–C_4H_8); 136 (M–SBu–*t*); 80 (CH_3SSH); 71 (C_5H_{11}); 57 (C_4H_9, 100%); 45 (CSH); 41 (C_3H_5)

(*continued*)

TABLE 2 (*continued*)

$(CH_3)_3SiCH_2SSSCF_3$ (retention time, 3.09 min)	M^+ = (not seen); 233 (M–F); 119 ($M-CF_3SS$); 104 [$(CH_3)_2SiCH_2$]; 90 (104-CH_2); 73 [$(CH_3)_3Si$, 100%]; 69 (CF_3); 63 (CSF); 59 [$(CH_3)_2SiH$]; 45 (CSH)
$(CH_3)_3SiCH_2SSCF_3$ (retention time, 1.53 min)	M^+ = 220; 201 (M–F); 147 (CH_2SSCF_3); 119 ($M-CF_3S$); 104 [$(CH_3)_2SiCH_2S$]; 90 (104-CH_2); 82 (CSF_2); 73 [$(CH_3)_3Si$, 100%]; 69 (CF_3); 63 (CSF); 59 [$(CH_3)_2SiH$]; 45 (CSH)
$(CH_3)_3SiCH_2SCF_3$ (retention time, 1.07 min)	M^+ = 188; 169 (M–F); 119 ($M-CF_3S$); 115 [$M-(CH_3)_3Si$]; 104 [$(CH_3)_2SiCH_2S$]; 96 ($C_2H_2F_2S$, 100%); 77 (96-F); 73 [$(CH_3)_3Si$]; 69 (CF_3); 63 (CSF); 59 [$(CH_3)_2SiH$]; 45 (CSH)
$[(CH_3)_3SiCH_2]_2$ (retention time, 1.47 min)	M^+ = 174; 159 ($M-CH_3$); 131 [$(CH_3)_3SiCH_2CH_2SiH_2$]; 115 [$M-(CH_3)_2SiH$]; 86 [$(CH_3)_3SiCH_2CH_2$, 100%]; 58 (86-C_2H_4); 45 (CSH)
$C_6H_5SSCF_3$ (retention time, 6.20 min)	M^+ = 210; 141 (C_6H_5SS); 109 (C_6H_5S, 100%); 82 (CSF_2); 77 (C_6H_5); 69 (CF_3); 45 (CSH)
$C_6H_5SCF_3$ (retention time, 3.51 min)	M^+ = 178; 159 (M–F); 109 (C_6H_5S, 100%); 82 (CSF_2); 77 (C_6H_5); 69 (CF_3); 45 (CSH)
$C_6H_5C_6H_5$ (retention time, 10.22 min)	M^+ = 154 (100%); 77 (C_6H_5)

in the reaction of t-butyllithium with the substrate is attributable to the presence of an impurity, namely pentyllithium, in the organolithium reagent. The mass spectra of CF_3SSCH_3 and CF_3SSSCH_3 have already been reported by others [15].

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