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GAS-PHASE THERMOLYSIS OF ARYL *TERT*-BUTYL DISULPHIDES

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The pyrolysis kinetics of RC_6H_4SS-*t*-C_4H_9 (R=H, *p*-NO_2, *p*-Cl, *p*-F) were determined at 390–450 °C and 7–15 Torr in a stirred-flow reactor using toluene as carrier gas. The reaction products were 95% isobutene, 5% isobutane and the corresponding RC_6H_4SSH disulphanes. The first-order rate constants, k (s^{-1}), based on isobutene production, followed the Arrhenius equations: phenyl *tert*-butyl disulphide, $k = 10^{13\cdot49 \pm 0\cdot31}$ $\exp[(-182 \pm 4\ \mathrm{kJ\ mol^{-1}})(RT)^{-1}$; pnitrophenyl *tert*-butyl disulphide, $k = 10^{13\cdot46 \pm 0\cdot32}$ $[\exp(-185 \pm 5\ \mathrm{kJ\ mol^{-1}})(RT)^{-1}]$; *p*-chlorophenyl *tert*-butyl disulphide, $k = 10^{14\cdot44 \pm 0\cdot66}$ $[\exp(-196 \pm 9\ \mathrm{kJ\ mol^{-1}})(RT)^{-1}]$; *p*-fluorophenyl *tert*-butyl disulphide, $k = 10^{10\cdot80 \pm 0\cdot16}$ $[\exp(-144\cdot5 \pm 2\ \mathrm{kJ\ mol^{-1}})(RT)^{-1}]$. The observed reactivities, within the above temperature range, follow the order *p*-F > H > *p*-Cl > *p*-NO_2. A four-centre, cuadrupolar cyclic transition state mechanism is proposed for the formation of the isobutene and aryldisulphane products. The optimized ground-state molecular geometries of the reactants were calculated by using the MINDO/3 procedure.

INTRODUCTION

Very few examples have been reported of the gas-phase pyrolysis of disulphides. Many years ago,[1] dimethyl disulphide was found to decompose by an overall complex free radical reaction. Di-*tert*-butyl disulphide, on the other hand,was found[2] to pyrolyse in a stirred-flow reactor to yield hydrogen disulphide and isobutene as main reaction products. It was suggested that these were primary products generated by consecutive unimolecular elimination of two molecules of isobutene, via four-centre cyclic transition states. About 5% isobutene, found also as a product, was attributed to the formation of *tert*-butyl radicals by a parallel minor C—S bond fission process.

Bock and Mohmand[3] used a photoelectron spectrometer to identify the products of a series of alkyl disulphides, pyrolysed at 690–840 K and a pressure of 0·1 Torr (1 Torr = 133·3 Pa). For the formation of hydrogen sulphide, alkenes and free sulphur, they proposed a chain reaction scheme involving thioalkyl radicals. This mechanism was considered to proceed by an initial S—S bond fission and by the decomposition of alkanethiol products formed by hydrogen abstraction by these radicals from the parent disulphide. In the case of di-*tert*-butyl disulphide pyrolysis, they did not report hydrogen disulphide as reaction product. Disulphide photolysis studies [4,5] have shown that C—S and S—S homolytic bond fissions are feasible in gas and condensed phases. Direct photolysis of disulphides proceeds by S—S bond cleavage and thioalkyl radical formation. In liquid-phase sensitized photolysis, C—S bond cleavage is a major reaction path. No evidence of the fate of the perthiyl radicals, however, was reported, although it has been assumed[5] that they end up as disulphane.

Since the unimolecular elimination of isobutene and hydrogen disulphide from di-*tert*-butyl disulphide[2] is the only example reported in the literature, this work was devoted to the study of the pyrolysis of phenyl *tert*-butyl disulphide (PTBD) *p*-nitrophenyl *tert*-butyl disulphide (NPTBD), *p*-chlorophenyl *tert*-butyl disulphide (CPTBD) and *p*-fluorophenyl *tert*-butyl disulphide (FPTBD) and examination of the mechanisms and substituent effects on the stabilization of a possible four-centre cyclic transition state.

EXPERIMENTAL

The aryl alkyl disulphides were synthesized as reported in the literature.[6,7] NPTBD and CPTBD were purified by vacuum sublimation (m.p. 60–62 and 33–35 °C, respectively). FPTBD was purified by reduced-pressure

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distillation (b.p. 60–63 °C/0·8 Torr). The reactant structures were confirmed by gas chromatography mass spectrometry using a Kratos RFA25 instrument fitted with a 30 m × 0·254 mm i.d. DB-1 fused-silica capillary column. This analysis indicated their purity to be better than 98%. NMR spectra were obtained on a Bruker AM300 instrument. The disulphides were pyrolysed by injecting 10 ml of 0·05–0·07 M solutions in toluene in a stirred-flow reactor[8] over periods of 20–30 min. Toluene was used as the carrier gas because it is known to be a good hydrogen atom source for inhibiting radical chain reactions. The experimental technique, reaction order measurement and rate coefficient calculation have been described previously.[9]

RESULTS

Over the temperature range 390–450 °C at total pressures between 7 and 15 Torr and with residence times below 2 s, the disulphides yielded the distribution of gas products shown in Table 1, plus C_2—C_3 hydrocarbons in trace amounts. The liquid products, collected at −78 °C, contained, in addition to the unreacted disulphide, the corresponding aryl disulphane. This could be titrated potentiometrically with 0·1 M silver nitrate solution,[10] as Table 2 shows for phenyl and *p*-nitrophenyl disulphane. The mass spectra of these fractions showed the presence of the symmetrical disulphides $(RC_6H_4S)_2$ and elemental sulphur after they had been standing overnight at room temperature.

The order for the consumption of the reactants was 1·0 ± 0·1 for NPTBD and 0·92 ± 0·03 for FPTBD, for 1·8- and 2.7-fold increases in the reactant inflow, respectively, at 430 °C. For PTBD, the order at 410 °C for a four-fold increase in reactant inflow was 1·06 ± 0·06. These orders were obtained from the least-squares plot shown in Figure 1. An order of one was assumed for all the disulphides. Tables 3–6 show the temperature variation of the rate coefficients, and also the experimental conditions, for half of the runs made for PTBD, NPTBD, CPTBD and FPTBD. Least-squares linear fits of the respective rate coefficients produced the Arrhenius parameters given in Table 7. The error limits in all the least-squares correspond to the standard error.[11]

Table 1. Gas products distribution

Reactant	Temperature range (°C)	i-C_4H_8[a] (%)	i-C_4H_{10}[a] (%)	H_2S[b] (%)
PTBD	390–440	94 ± 1	6 ± 1	~1
NPTBD	420–460	95 ± 1	5 ± 1	16 ± 2
CPTBD	390–421	95 ± 1	5 ± 1	9 ± 3
FPTBD	400–450	94 ± 1	6 ± 1	7 ± 3

[a] Only in C_4 hydrocarbon mixture.
[b] In total gas moles.

Table 2. Aryl disulphane and C_4 hydrocarbon measurements

Reactant	Temperature °C	Amount (mol × 10^4)		
		i-C_4H_8	—SSH	Total C_4
PTDB	390·9	3·04	3·50	3·17
	390·5	3·33	3·45	3·47
	411·0	2·08	2·20	2·23
	410·7	2·48	2·90	2·66
	410·5	2·15	2·20	2·31
	420·4	3·93	3·50	4·17
	429·3	5·16	5·55	5·48
	429·6	5·26	5·80	5·69
	439·8	6·05	7·61	6·49
NPTBD	430·8	1·31	1·60	1·39
	430·9	2·32	2·75	2·46

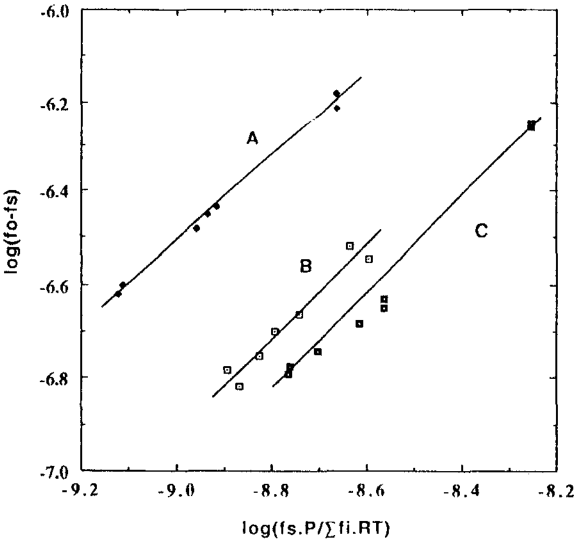

Figure 1. Reaction order plots. (A) FPTBD; (B) NPTBD; (C) PTBD. f_0 = reactant inflow; f_s = reactant outflow; Σf_i = total outflow; P = total pressure; R = gas constant; T = absolute temperature

Table 3. Stirred flow pyrolysis of phenyl *tert*-butyl disulphide

Temperature (°C)	k(10^4 s^{-1})[a]	θ(s)[b]	r(C_4H_8)[c] (%)	P(Torr)	f_R° × 10^8[d]	f_c/f_R°[e]
390·9	1722	1·799	23·65	12·7	56·3	69·5
400·9	2554	0·814	17·21	12·3	115·4	72·0
400·9	2446	0·848	17·18	9·82	92·5	68·5
410·1	3530	0·649	18·65	9·62	114·1	70·1
410·2	3977	0·642	20·33	8·05	74·6	91·2
420·7	6638	0·659	30·44	8·33	107·9	62·0
420·6	6651	0·641	29·90	7·84	94·1	68·9
429·6	10513	0·634	40·01	8·81	100·9	72·0
430·4	9750	0·588	36·46	9·24	134·4	60·9
439·8	14778	0·592	46·65	8·33	109·0	66·5
439·2	15235	0·568	46·40	8·22	98·9	75·5

[a] Rate coefficient.
[b] Residence time.
[c] Percentage reaction from isobutene measurement.
[d] Reactance inflow (mol s^{-1}).
[e] Toluene to reactant flow ratio.

Table 4. Stirred flow pyrolysis of *p*-nitrophenyl *tert*-butyl disulphide

Temperature (°C)	k(10^4 s^{-1})[a]	θ(s)[b]	r(C_4H_8)[c] (%)	P(Torr)	f_R° × 10^8[d]	f_c/f_R°[e]
421·0	3088	0·758	18·97	13·9	129·8	74·9
430·6	5240	0·524	21·90	9·23	131·6	68·7
430·6	5120	0·529	21·63	10·1	71·7	137·0
430·3	4899	0·588	22·38	9·34	83·9	99·6
430·8	5123	0·626	25·75	10·4	89·1	97·9
440·5	7787	0·578	31·05	9·31	66·5	126·0
440·3	8031	0·567	31·28	8·99	84·7	97·2
449·9	11928	0·577	40·75	8·95	88·4	89·7
449·8	10478	0·563	37·12	8·68	56·8	139·0
459·7	18236	0·473	46·29	8·77	88·4	106·0
458·6	16518	0·561	48·11	8·23	43·2	172·0

[a–e] See Table 3.

Table 5. Stirred flow pyrolysis of *p*-chlorophenyl *tert*-butyl disulphide

Temperature (°C)	k(10^4 s^{-1})[a]	θ(s)[b]	r(C_4H_8)[c] (%)	P(Torr)	f_R° × 10^8[d]	f_c/f_R°[e]
389·8	1094	1·97	17·70	14·6	41·9	99·4
389·8	881	1·94	14·61	14·4	41·7	99·4
390·2	832	1·94	13·90	14·5	67·3	61·7
390·1	934	1·94	15·37	14·5	67·2	61·7
401·1	2103	1·01	18·35	14·4	86·8	90·6
400·5	1900	1·19	18·45	12·6	64·2	90·6
400·2	1818	1·06	16·21	13·3	84·8	80·6
408·7	3137	0·777	19·61	12·0	114·5	73·0
410·5	3063	0·784	19·36	12·6	118·9	73·0
410·4	2991	0·776	18·83	12·7	89·3	99·0
409·8	3051	0·763	18·89	12·7	90·9	99·0
420·8	4661	0·824	27·74	8·41	45·6	120·0
421·2	4793	0·802	27·77	8·78	70·0	83·2
421·3	4892	0·792	27·94	8·57	69·2	83·2

[a–e] See Table 3.

Table 6. Stirred flow pyrolysis of *p*-fluorophenyl *tert*-butyl disulphide

Temperature (°C)	$k(10^4\,\mathrm{s}^{-1})$[a]	θ(s)[b]	$r(C_4H_8)$[c] (%)	*P*(Torr)	$f_R^\circ \times 10^8$[d]	f_s/f_R°[e]
400·7	3848	0·841	24·46	11·6	85·2	89
400·3	4056	0·814	24·82	13·5	118·8	77
410·3	5364	0·822	30·59	11·6	80·4	95
410·4	5580	0·796	30·76	11·2	122·7	61
420·1	7658	0·549	29·61	7·34	87·1	82
418·8	8058	0·496	28·55	7·97	145·9	58
430·0	11680	0·495	36·65	8·28	168·5	52
430·2	12063	0·477	36·51	8·76	61·1	159
439·8	17604	0·480	45·82	8·76	146·9	64
440·1	17023	0·482	45·08	9·35	102·9	98
450·4	23370	0·500	53·87	8·00	105·6	77
450·7	22626	0·479	52·00	8·56	96·0	97

[a–e] See Table 3.

Table 7. Kinetic parameters for RSS-*tert*-butyl

R	E_a (kJ mol^{-1})	Log *A*	$\Delta S^{\neq}$ (J mol^{-1}K^{-1})[a]	$k(10^2\,\mathrm{s}^{-1})$ 390 °C	$k(10^2\,\mathrm{s}^{-1})$ 450 °C	k_r[b]	Ref.
C_6H_5	182 ± 4	13·49 ± 0·31	−2·3	14	222	1·7	This work
p-$NO_2C_6H_4$	185 ± 5	13·46 ± 0·32	−2·9	8	126	1	This work
p-ClC_6H_4	196 ± 9	14·44 ± 0·66	15·9	10	193	1·2	This work
p-FC_6H_4	145 ± 2	10·80 ± 0·16	−53·8	26	231	3·2	This work
t-C_4H_9[c]	184 ± 4	14·6 ± 0·4	18·9	65	1030	8	2
t-C_4H_9[d]	177 ± 2	13·57 ± 0·22	−0·8	26	310	2·2	2

[a] At 450 °C.
[b] Relative coefficient at 390 °C.
[c] Flow system measurements.
[d] Static system measurements

DISCUSSION

The stoichiometry for the pyrolysis of the aryl *tert*-butyl disulphides may be represented by the equation

$$RC_6H_4SS\text{-}t\text{-}C_4H_9 \rightarrow RC_6H_4SSH + i\text{-}C_4H_8 \qquad (1)$$

Langer and Hyne[12] found that the aryl disulphanes decompose on standing by a complex radical mechanism, the overall result of which they represented by the equation

$$3RC_6H_4SSH \rightarrow RC_6H_4S_xC_6H_4R' + RC_6H_4SH + S \qquad (2)$$

This decomposition is very sensitive to impurities and to the surface of glass. The formation of polysulphanes, thiols and sulphur occurs through a number of intermediate higher sulphanes of the type $RC_6H_4S_xH$ and HS_xH. The hydrogen sulphide measured in the gas products (Table 1) is most likelv to be formed from disulphane decomposition [equation (2)] and not as a primary pyrolysis product. The detection of free sulphur and the corresponding symmetrical disulphides in the aged liquid fractions confirms this assumption. It is unlikely that the two reaction products in equation (1) are formed by the intervention of radicals originating from homolytic C—S or S—S bond fission. A unimolecular mechanism, involving a four-centre cuadropolar cyclic transition state,[13] similar to that proposed for homologous sulphides and ethers,[9] seems to be the most likely path for product formation in equation (1). The fact that the mass spectra of these disulphides clearly show the peak of *m*/*z* corresponding to the aryl disulphane [C_6H_5SSH, $m/z = 142$, 96%; *p*-ClC_6H_4SSH, *m*/*z* 176, 64%; *p*-FC_6H_4SSH, *m*/*z* 160, 48%; *p*-$NO_2C_6H_4SSH$, *m*/*z* 187, 9·2%; base peak, C_4H_9 *m*/*z* 57; 70 eV) confirms that the 1–3 hydrogen transfer mechanism occurs also under electron impact conditions

Table 8 shows some relevant parameters from the

Table 8. Selected parameters from MINDO/3 optimized molecular geometries

Parameter	PTBD	FPTBD	NPTBD
$\Delta H_f{}^{\circ}{}_{298}$ (kJ mol^{-1})	−8·57	50·65	96·75
Ionization potential (eV)	7·95	8·02	8·44
Bond angles (°)			
C3S1—S2C16 (dihedral)	109·26	91·508	111·65
O27N26—C25C21 (dihedral)	—	—	90·225
C3S1S2	117·56	120·01	117·52
C16S2S1	116·91	128·38	116·83
O27N26C25	—	—	114·12
Bond lengths (Å)			
S-1—S-2	2·1017	2·1067	2·1057
S-1—C-3	1·8054	1·8051	1·8078
S-2—C-16	1·7357	1·7776	1·7295
C-8—H-9	1·1214	1·1106	1·1104
C-12—H-13	1·1108	1·1262	1·1257
C-3—C-8	1·5148	1·5081	1·5086
C-3—C-12	1·5087	1·5145	1·5143
Interatomic distances (Å)			
S-1 to H-9	2·0852	2·8907	2·8825
S-1 to H-13	2·8955	1·9922	1·9962
Net atomic charges (atomic units)			
S-1	−0·0857	0·0416	0·0560
S-2	−0·1649	0·1859	1·1826
C-3	0·1566	0·1486	0·1602
C-8	0·0625	0·0504	0·0470
C-12	0·0502	0·0609	0·0572
C-16	0·1580	0·0976	0·1884
C-25	−0·0235	0·4108	0·1986
H-9	0·006	−0·0138	0·0098
H-13	−0·0155	0·0124	0·0146
N-26	—		1·1161
O-27	—	—	−0·5825
O-28	—	—	−0·5840
F-26	—	0·3359	—

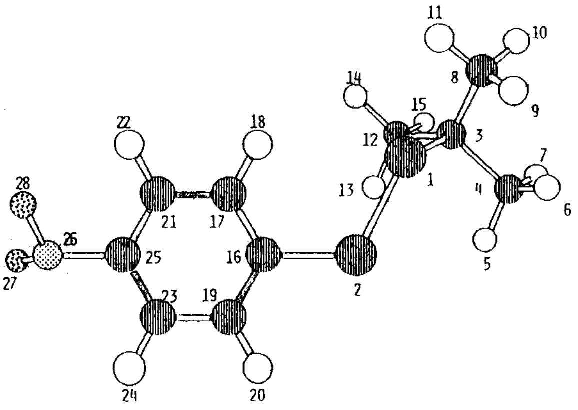

Figure 2. Molecular geometry of NPTBD (see Table 8)

optimized ground-state molecular geometries of PTBD, FPTBD and NPTBD, obtained by using the MINDO/3 calculation procedure.[14] The corresponding atom numbers are given in Figure 2. These calculations show that only one H atom on the *tert*-butyl moiety bears a net positive charge. This H atom is bonded to the methyl C atom having the lowest positive charge, while the tertiary C atom has the highest positive charge. Both S atoms have net negative charges. In each of the three conformations, the positively charged H atom is also the one with the shortest interatomic distance to the S atom bonded to the *tert*-butyl group. These net atomic charge distributions resemble that expected for the atoms involved in the proposed polar four-centre cyclic transition state. The necessary conformational changes involving interatomic distances and bond angles can easily be realized in a reactant molecule energized about 180 kJ mol^{-1} above the ground state.

Table 7 gives the rate coefficients, calculated at 390 and 450 °C by using the respective Arrhenius parameters, for the aryl *tert*-butyl disulphides, and also those for di-*tert*-butyl disulphide.[2] Within this temperature range, the following reactivity order was observed: FPTBD > PTBD > CPTBD > NPTBD. FPTBD is 1·9, 2·6 and 3·2 times more reactive than PTBD, CPTBD and NPTBD, respectively. Replacement of *p*-H by F in PTBD produces a decrease of 37 kJ mol^{-1} in E_a and hence a less energetic, very tight transition state, as suggested by the low value of the entropy of activation. Although replacement of H by either *p*-NO_2 or *p*-Cl produced changes in the activation parameters within the experimental error, still the rate-decreasing effect of these substituents (0·57 and 0·71, respectively) was evident. These substituent effects would bear upon the C—H bond-making and rate-determining C—S bond-breaking steps in a polar transition state. The $+M$ effect of a *p*-F atom in the benzene ring would increase a partial negative charge on the distal S atom, thus making the 1–3 shift of a partial positive H atom more facile. The $-M$ effect of the *p*-Cl and *p*-NO_2 groups, however, tends to stabilize the polarization of the *tert*-butyl C—S bond in the transition state, owing to stabilization of a partial negative charge in the latter atom. These effects in the disulphides, although similar to those in analogous ethers and sulphides,[9] are very much diminished by the high polarizability of the S atom (3.48 Å^3),[15] which can stabilize the partial charges in polar transition states. The transition state model of Haugen and Benson[13] for this type of reaction, however, may explain the observed behaviour in the pyrolyses of the present alkyl aryl disulphides.

In the light of the values of the activation parameters for the aryl *tert*-butyl disulphides shown in Table 7, it is still difficult to choose between the activation parameters obtained in the flow or in the static system measurements as being the more representative for di-*tert*-butyl disulphide. It seems evident, once the statistical factor is taken into account, that the latter is at least as reactive as FPTBD.

Since the presence of up to 6% isobutane in the products means its formation from *tert*-butyl radicals, it is worth reconsidering the estimated C—S and S—S bond dissociation energies (*BDE*) in disulphides. Recent measurements[16] made by an electron impact technique gave *BDE*(MeSS—R) = 237–220 kJ mol^{-1} for R = Me, Et, *i*-Pr and *t*-Bu. For the symmetrical tetrasulphides the *BDE*(RSS—SSR) fell within the narrow range 136–138 kJ mol^{-1}. Table 9 gives some relevant enthalpies of formation for the estimation of the *BDE*(C—S) and *BDE*(S—S) [equations (3)–(12)] (ΔH°_{R298}, kJ mol^{-1}):

$$C_6H_5SS\text{-}t\text{-}C_4H_9 \rightarrow C_6H_5SS^\cdot + t\text{-}C_4H_9^\cdot \quad 263 \qquad (3)$$

$$\rightarrow C_6H_5S^\cdot + t\text{-}C_4H_9S^\cdot \quad 276 \qquad (4)$$

Table 9. Enthalpies of formation

Species	$\Delta H_f^\circ{}_{298}$(kJ mol^{-1})	Ref.
C_6H_5SS-*t*-C_4H_9	−8.57	–[a]
(*t*-$C_4H_9S)_2$	−198.7	17
CH_3SS-*t*-C_4H_9	−112	16
AllylSSallyl	129	18
AllylSS-*t*-C_4H_9	−36.4	18
CH_3SSCH_3	−24.3	16
t-$C_4H_9SS^\cdot$	−19.3	16
t-$C_4H_9S^\cdot$	(29)	—[a]
$C_6H_5SS^\cdot$	(205)	—[a]
$C_6H_5S^\cdot$	238 ± 8	19
$CH_3SS^\cdot$	68.6	16,20
$CH_3S^\cdot$	143 ± 8	19
$CH_3^\cdot$	146.9 ± 0.6	21
t-$C_4H_9^\cdot$	49 ± 2	22
AllylSS$^\cdot$	157	18
AllylS$^\cdot$	195	18
Allyl$^\cdot$	163.2	21

[a] Estimated by the authors by group additivity method (Ref. 23), values in parentheses.

$$CH_3SSCH_3 \rightarrow CH_3SS^\cdot + CH_3^\cdot \quad 240 \qquad (5)$$

$$\rightarrow 2\ CH_3S^\cdot \quad 310 \qquad (6)$$

$$(t\text{-}C_4H_9S)_2 \rightarrow t\text{-}C_4H_9SS^\cdot + t\text{-}C_4H_9^\cdot \quad 228 \qquad (7)$$

$$\rightarrow 2\ t\text{-}C_4H_9S^\cdot \quad 257 \qquad (8)$$

$$CH_3SS\text{-}t\text{-}C_4H_9 \rightarrow CH_3SS^\cdot + t\text{-}C_4H_9^\cdot \quad 230 \qquad (9)$$

$$\rightarrow CH_3S^\cdot + t\text{-}C_4H_9S^\cdot \quad 284 \qquad (10)$$

$$\text{allylSSallyl} \rightarrow \text{allylSS}^\cdot + \text{allyl}^\cdot \quad 191 \qquad (11)$$

$$\rightarrow 2\ \text{allylS}^\cdot \quad 261 \qquad (12)$$

The above enthalpies, although approximate within ±20 kJ mol^{-1}, suggest that the homolytic C—S bond fission in disulphides is at least as feasible as the S—S bond fission.

The fate of the radicals formed in equation (3) would most likely be disproportionation for the *tert*-butyl radicals and hydrogen abstraction for the perthiyl radicals, as suggested previously.[2]

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