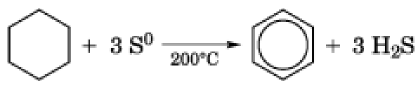
Kirk-Othmer Encyclopedia of Chemical Technology.

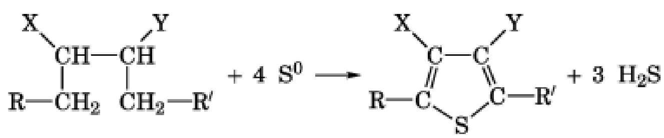
SULFURIZATION AND SULFURCHLORINATION

Sulfur reacts with alkanes to either dehydrate (eq. **1**), oxidize, forming carbon disulfide and hydrogen sulfide (eq. 2), or cyclize, forming thiophenes (eq. **3**). The products of alkane sulfurization depend on the temperature, the time at the temperature, and the structure of the hydrocarbon (1).



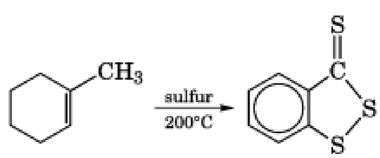
(1)

$$C_xH_y \xrightarrow[>500^\circ C]{\text{sulfur}} x\ CS_2 + y/2\ H_2S \qquad (2)$$



(3)

Generally, unsaturated compounds, eg, alkenes and natural fats and their derivatives, are much more reactive toward sulfur than alkanes. Sulfur reacts with unsaturated compounds at temperatures of 120–215°C, forming products that are usually dark and often viscous cross-linked mixtures of dithiole-3-thiones (eq. **4**) (2) and sulfides (Table 1) (3).



(4)

The mechanisms for the reaction of sulfur with alkanes and unsaturated compounds are highly speculative, being strongly influenced by the specific structure of the substrate and by the conditions (particularly temperature) of reaction. Alkane (4), olefin (5), animal fat (6), and vegetable oil (7) sulfurization have been extensively studied because these reactions are models for vulcanization. Moreover, the products are used as lubricant additives.

Sulfur reacts with mercaptans in the presences of basic catalysts at temperatures of 75–105°C, forming sulfides. These sulfides are usually light in color and are formed without cross-linking. The sulfurization of mercaptans leads to di-, tri-, or higher polysulfides, depending on the mole ratio used (eqs. 5 and 6). An extensive list of references to the sulfurization of mercaptans is available (8).

$$2\ R—S—H + 2\ S \xrightarrow[-H_2S]{\text{catalyst}} R—S_3—R \qquad (5)$$

Table 1. Products of the Reaction of 1-Octene with Sulfur at 140°C

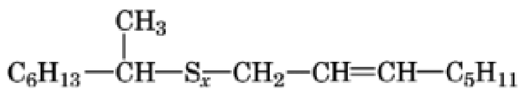
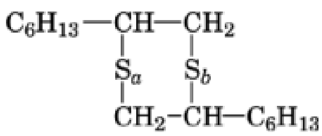
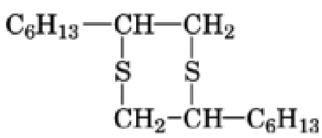
Product		Quantity, %
	av x = 6.7	25
	av $(a + b)$ = 6.7	30
$C_8H_{17}—S—C_8H_{17}$ + $C_8H_{17}—S—C_8H_{15}$		15
$C_8H_{17}—S_a—C_8H_{16}—S_b—C_8H_{17}$	av $(a + b)$ = 4.7	15
 + $C_8H_{17}—S—C_8H_{16}—S—C_8H_{17}$		15

Table 2. Chemical and Physical Properties of Sulfurized and Sulfurchlorinated Unsaturated Compounds and Mercaptans

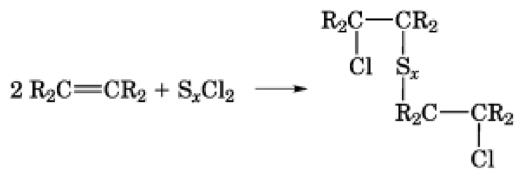
Product[a] designation	Sulfur, wt %	Chlorine, wt %	Active sulfur, wt %	Copper strip tarnish test, 10 wt % in oil	Viscosity, mm^2/s (=cSt) 40°C	Viscosity, mm^2/s (=cSt) 100°C	Density, at 25°C, g/cm^3	Total acid number, mg KOH/g	Pour point, °C
Base 10-L[b]	10.0	0	0	1B	1100	80	0.98	25	18
Base 10-SE[c]	10.0	0	0	1B	20	4	0.94	5	10
Base 14-L[d]	14.0	0	4	4a	1700	100	0.99	25	27
Base 401[d]	40.0	0	25	4c	80	10	1.07	7	-50
Base L-66[e]	5.5	5.5	0	1B	1800	100	0.99	5	10
Sulperm 18[f]	18.0	0	8	4a	600	55	1.02	12	16
Sulperm 110[f]	10.0	0	0	1B	500	40	0.98	8	10
DTNPS[g]	37.0	0	25	4c	35		1.04	5	-50
DTBTS[h]	44.0	0	0	1B	3		1.00	0	$<$ -60

[a]Products and properties submitted by Keil Chemical Division of Ferro Corp.
[b]Based on animal fat.
[c]Based on methyl ester of vegetable oil.
[d]Based on olefin.
[e]Sulfurchlorinated animal fat.
[f]Based on a mixture of animal and vegetable oils plus synthetic esters.
[g]Di-*t*-nonyl pentasulfide (DTNPS) is based on mercaptan.
[h]Di-*t*-butyl trisulfide (DTBTS) is based on mercaptan.

$$2\,\mathrm{R{-}S{-}H} + 4\,\mathrm{S} \xrightarrow[-\mathrm{H_2S}]{\text{catalyst}} \mathrm{R{-}S_5{-}R} \qquad (6)$$

Sulfurization of unsaturated compounds in the presence of hydrogen sulfide also affords polysulfides (9). It is postulated that this reaction forms the mercaptan *in situ*, which then further reacts to form the polysulfide (see Sulfur compounds).

Sulfur monochloride [10025-67-9], S_2Cl_2, and sulfur dichloride,SCl_2, react with unsaturated materials, forming products that are cross-linked by sulfur but which also contain chlorine (eq. **7**) (10).



(7)

Sulfur monochloride and sulfur dichloride also react with mercaptans, yielding tetra- and trisulfides (eqs. 8 and 9) (11).

$$2\,\mathrm{R{-}S{-}H} + \mathrm{S_2Cl_2} \longrightarrow \mathrm{R{-}S_4{-}R} \qquad (8)$$

$$2\,\mathrm{R{-}S{-}H} + \mathrm{SCl_2} \longrightarrow \mathrm{R{-}S_3{-}R} \qquad (9)$$

1. Properties

Properties of typical commercial sulfurized unsaturated compounds and mercaptans are listed in Table 2.

2. Uses

Sulfurized and sulfurchlorinated unsaturated compounds and mercaptans are used as lubricant additives (antiwear, friction modification, load-carrying, extreme pressure and temperature, corrosion inhibition, and antioxidants), refinery catalyst regeneration compounds, steel processing (annealing) aids, and vulcanization catalysts (see Lubrication and lubricants).

3. Manufacture

Sulfurization of unsaturated compounds and mercaptans is normally carried out at atmospheric pressure, in a mild or stainless steel, batch-reaction vessel equipped with an overhead condenser, nitrogen atmosphere, an agitator, heating media capable of 120–215°C temperatures and a scrubber (typically caustic bleach or diethanolamine) capable of handling hydrogen sulfide. If the reaction involves the use of H_2S as a reactant or the olefin or mercaptan is a low boiling material, a stainless steel pressurized vessel is recommended.

Sulfurchlorination of unsaturated compounds or mercaptans is normally carried out at atmospheric pressure in a glass-lined reaction vessel because of the potential to liberate HCl during the reaction. The sulfurchlorination vessel is equipped with a cooling jacket or coils (very exothermic reaction), a nitrogen or dry air sparging system, an overhead condenser, and a caustic or bleach scrubber. If one of the reactants (olefin or mercaptan) is a low boiling material, ie, isobutylene, a glass-lined pressure vessel is recommended.

4. Health and Safety Factors

Sulfurized and sulfurchlorinated unsaturated compounds or mercaptans are normally considered nonhazardous. These materials may, however, liberate H_2S and HCl at elevated ($> 200°C$) temperatures and during combustion.

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Related Articles

Sulfur compounds; Lubrication and lubricants