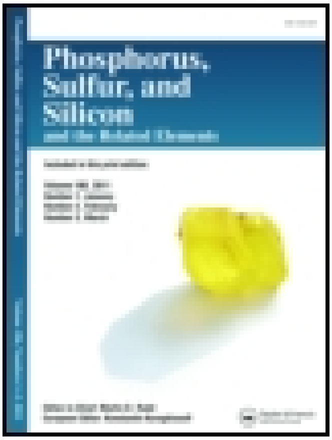

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James E. Shaw [a] & Marilyn G. McAfee [a]
[a] Phillips Petroleum Company , Research Center Building 92-F, Bartlesville, Oklahoma, 74004

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OXIDATION OF THIOLS TO DISULFIDES BY ELEMENTAL SULFUR WITHOUT CONTAMINATION BY HIGHER POLYSULFIDES

JAMES E. SHAW* and MARILYN G. McAFEE

Phillips Petroleum Company, Research Center, Building 92-F, Bartlesville, Oklahoma 74004

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Dialkyl disulfides were prepared in near quantitative yield by oxidation of alkanethiols with elemental sulfur using NaOH and ethoxylated alcohols as catalysts. Tergitol® 15-S-7 was one of several ethoxylated alcohols which was used. Contamination by trisulfides was essentially eliminated in the disulfide products. The ratios of disulfide to trisulfide ranged from 100/0 to 99.6/0.4 for reactions with primary and secondary alkanethiols (100% excess) such as 1-propanethiol, 1-octanethiol, 2-propanethiol, and 2-butanethiol. The process did not work for tertiary alkanethiols such as 2-methyl-2-propanethiol where the trisulfide was greatly favored.

Keywords: oxidation; thiols; disulfides; trisulfides; sulfur

Althought thiols are readily oxidized to disulfides using elemental sulfur and a basic catalyst (eq 1), a major problem with the method is that significant amounts of trisulfides and other higher polysulfides are also produced.[1–3] This has caused the sulfur method to be generally excluded in reviews[4–6] of synthetic methods for disulfides.

$$2\ \text{R-SH} + \text{S} \rightarrow \text{R-S-S-R} + \text{H}_2\text{S} \qquad \text{(eq 1)}$$

In our work on the preparation of disulfide polymers,[7] we found a catalyst system which essentially eliminates higher polysulfides and provides disulfides in near quantitative yields. We have now investigated this in more detail for the conversion of simple thiols to disulfides. The catalyst system is a mixture of NaOH and an ethoxylated alcohol, $RO(CH_2CH_2O)_xH$. Ethoxylated alcohols which were used were Tergitol®

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* Corresponding authors.

15-S-5 and 15-S-7 (Union Carbide) where R is a mixture of C_{11}-C_{15} secondary alkyl groups and x is a number which averages 5 and 7, respectively, and Neodol® 23–3 and 23–6.5 (Shell Chemical) where R is a mixture of C_{12}-C_{13} primary alkyl groups and x is a number which averages 3 and 6.5, respectively.

Table I shows the relative percentages of disulfides and trisulfides produced at different reaction times when various thiols (100% excess) and sulfur were reacted using NaOH and Tergitol® 15-S-7 as catalysts. Oxidation of 1-propanethiol and 1-octanethiol gave 99.9–100% disulfide relative to only 0–0.1% trisulfide after 1 hr at 50 °C. Yields (GC) of disulfide based on sulfur were 99.7–99.8%. In contrast, when triethylamine was used as catalyst with 1-octanethiol under the same conditions, the percentages of di- and trisulfides after 1 hr were 78 and 22%, respectively. When the amount of excess 1-propanethiol was reduced from 100% to 50% in a run with NaOH and Tergitol® 15-S-7, the disulfide to trisulfide ratio instead of being 99.9/0.1 was 98.0/2.0 after 1 hr and 98.4/1.6 after 2 hr showing that a lower excess of thiol did not result in very low trisulfide. Secondary alkanethiols such as 2-propanethiol and 2-butanethiol also gave excellent results using NaOH and Tergitol® 15-S-7 as catalysts, but longer reaction times were required to convert the trisulfide byproduct to disulfide (Table I). Yields of disulfide were greater than 99%. Poor results were observed with tertiary alkanethiols such as 2-methyl-2-propanethiol. Reaction of this (100% excess) with sulfur using NaOH and Tergitiol® 15-S-7 as catalysts gave only a 2.5% yield of disulfide after 3 hr and a 3.2% yield after 6 hr. The major product was the trisulfide (95.6% yield). Steric hinderance must prevent disulfide formation in the tertiary thiol case.

TABLE I Oxidation of thiols to disulfides by elemental sulfur using NaOH and Tergitol® 15-S-7 as catalysts[a]

alkanethiol[b]	*mole ratio of disulfide/trisulfide at different reaction times*		*% yield of disulfide*	
	1 h	*3 h*	*GC*	*isolated*
1-propanethiol	99.9/0.1	-	99.7	95
1-octanethiol	100/0	-	99.8	98
2-propanethiol	97.9/2.1	99.9/0.1	99.5	93
2-butanethiol	97.0/3.0	99.6/0.4	99.2	95
2-methyl-2-propanethiol	-	2.5/95.8[c]	2.5	-

[a] Tergitol obtained from Union Carbide Corp., 39 Old Ridgebury Rd., Danbury, CT 06817.
[b] Thiol present in 100% excess relative to sulfur.
[c] Ratio including tetrasulfide was 2.5/95.8/1.7.

Many different catalysts were studied in the reaction of 1-propanethiol with sulfur. Table II shows the results obtained with NaOH and different ethoxylated alcohols as well as NaOH and 18-crown-6 or Adogen® 464 which is methyltrialkyl (C_8-C_{10}) ammonium chloride. All ethoxylated alcohols (Tergitols and Neodols), which were tested, gave similar results. After 45 min at 50 °C, 99.6–99.9% disulfide was obtained relative to only 0.1–0.4% trisulfide. The order of addition of sulfur and thiol also appeared to have no effect. Table II shows which runs involved addition of sulfur to thiol or thiol to sulfur over an initial 2–5 min time period (also see Experimental). The ethoxylated alcohols gave superior results compared to poly(ethylene glycol). The crown ether, 18-crown-6, gave just as good results as the ethoxylated alcohols, but it is less attractive since ethoxylated alcohols are far cheaper and far less toxic. The quaternary alkyl ammonium salt, Adogen® 464, and NaOH was a good catalyst system, but tetramethylammonium hydroxide with a small amount of methanol was somewhat less effective. Larger alkyl groups are preferred as in Adogen® 464. Much less effective catalysts were triethylamine and NaOH with a small amount of methanol.

TABLE II Oxidation of 1-propanethiol to the disulfide by sulfur using different catalysts

catalysts	*sulfur and thiol*[a] *addition order*	*mole ratio of disulfide/trisulfide at different reaction times*	
		15 min	*45 min*
NaOH-Tergitol 15-S-5	A	99.5/0.5	99.8/0.2
NaOH-Tergitol 15-S-5	B	99.4/0.6	99.7/0.3
NaOH-Tergitol 15-S-7	A	99.4/0.6	99.7/0.3
NaOH-Tergitol 15-S-7	B	99.5/0.5	99.8/0.2
NaOH-Neodol 23–3[b]	A	99.7/0.3	99.9/0.1
NaOH-Neodol 23–6.5[b]	A	99.2/0.8	99.6/0.4
NaOH-poly(ethylene glycol)[c]	A	91.3/8.7	96.0/4.0
NaOH-18-crown-6	A	99.2/0.8	99.9/0. 1
NaOH-Adogen 464[d]	A	99.2/0.8	99.5/0.5
tetramethylammonium hydroxide in methanol	B	98.9/1.1	-
triethylamine	B	82/18	89/11
NaOH-methanol	B	41.4/58.6[e]	-

[a] A means initial addition of thiol to sulfur and B means initial addition of sulfur to thiol.
[b] Neodols® obtained from Shell Chemical Co., 1 Shell Plaza, Houston, TX 77002.
[c] Average molecular weight was 600.
[d] Adogen® obtained from Aldrich Chemical Co.
[e] Incomplete reaction of all sulfur using NaOH-methanol.

In the isolation of the disulfides, removal of NaOH and Tergitiol® 15-S-7 from the reaction mixture by washing with water was unsatisfactory due to the Tergitol® causing severe emulsion problems. Instead, disulfides were isolated by adding the reaction mixture to a short column of silica gel and eluting with hexane (or pentane). This removed the NaOH and Tergitol®, Hexane and excess thiol were then removed from the disulfide by evaporation under reduced pressure. Alternatively, after elution, the excess thiol was removed by extraction of the hexane solution with aqueous NaOH solution. However, this should be done after removal of Tergitol® on the silica gel column since it would cause emulsion problems.

The methods described in this paper make elemental sulfur a much more attractive reagent for conversion of thiols to disulfides since contamination by higher polysulfides is essentially eliminated.

EXPERIMENTAL

Dipropyl Disulfide

To a 250 mL, 3-necked flask equipped with a thermowell, magnetic stirring bar, pressure equalizing addition funnel, and condenser with N_2 inlet on top was added 0.26 g of 50% aqueous NaOH solution, 1.72 g of Tergitol® 15-S-7 (Union Carbide), and 5.00 g (0.156 g-atom) of elemental sulfur (powdered, flowers of sulfur). The 1-propanethiol (47.5 g, 0.624 mol), which was in excess (100%), was added in portions over 5 min with stirring and increasing the temperature over this time to 50 °C. CAUTION: Toxic hydrogen sulfide gas is evolved as a byproduct, and thus this reaction should be carried out in a hood. The reaction mixture was maintained at 50 °C, and small samples were taken for GC analysis (10 m by 0.53 mm ID HP-1 methyl siloxane capillary column, column temperature 50 °C initially, then 15 °C/min, injection port 200 °C, FID detector) at the desired times (Tables I and II). GC analysis of the final reaction mixture (48.2 g) after 1 hr at 50 °C showed that it contained 48.5% dipropyl disulfide along with excess 1-propanethiol. The yield (GC) of dipropyl disulfide based on elemental sulfur was 99.7%. All products were identified by comparison with authentic materials.

The dipropyl disulfide was isolated by adding the reaction mixture to a short column of 60 g of silica gel and eluting with hexane (or pentane). After removal of the NaOH and Tergitiol® 15-S-7 in this way, hexane and excess 1-propanethiol were removed by evaporation under reduced pressure to give 22.3 g (95% yield) of dipropyl disulfide. Severe emulsion problems were encountered if removal of NaOH and Tergitiol was attempted by washing with water.

In other runs with different catalysts where 1-propanethiol was added to the elemental sulfur, the procedure and amounts of reagents were the same except that the Tergitol® 15-S-7 was replaced by the same weight of another catalyst. However, in the case of Adogen® 464 only 1 g was used.

An alternative procedure involved the reverse addition of the elemental sulfur to the 1-propanethiol. To a 100 mL, 3-necked flask equipped with a thermowell, magnetic stirring bar, and condenser with N_2 inlet on top was added 0.052 g of aqueous 50% NaOH, 0.344 g of Tergitol® 15-S-7 (Union Carbide), and 9.50 g (0.125 mol) of 1-propanethiol. The mixture was heated to 50 °C with stirring. Then 1.00 g (0.0312 g-atom) of elemental sulfur (powdered, flowers of sulfur) was added in portions over 2 min (Caution: H_2S evolution). The reaction mixture was maintained at 50 °C for the times given in Tables I and II. The results were essentially identical to those of the initial procedure above. In the alternative procedure where sulfur was added to the thiol, runs with other catalysts were exactly the same except that the 50% NaOH and Tergitol was replaced by 0.073 g of triethylamine, 0.25 g of 20% tetramethylammonium hydroxide in methanol, or 0.386 g of 6.7% NaOH in methanol.

Bis(1-methylethyl) Disulfide

The procedure was the same as the initial procedure for dipropyl disulfide above except that the amounts of reagents were 0.30 g of 50% aqueous NaOH, 1.93 g of Tergitol® 15-S-7 (Union Carbide), 4.89 g (0.152 g-atom) of sulfur (powdered, flowers of sulfur), and 47.0 g (0.617 mol) of 2-propanethiol, and the reaction time at 50 °C was 3 h (Caution: H_2S evolution). Products were identified by comparison with authentic materials. The yield (GC) of bis(1-methylethyl) disulfide was 99.5%.

Bis(1-methylpropyl) Disulfide

The procedure was the same as the procedure for bis(1-methylethyl) disulfide except that the amounts of reagents were 0.30 g of 50% aqueous NaOH, 1.93 g of Tergitol® 15-S-7, 4.89 g (0.152 g-atom) of sulfur, and 55.0 g (0.610 mol) of 2-butanethiol, and the reaction time at 50 °C was 3 h (Caution: H_2S evolution). Products were identified by comparison with authentic materials. The yield (GC) of bis(1-methylpropyl) disulfide was 99.2%.

Bis(2-methylpropyl) Disulfide

The procedure was the same as for bis(1-methylpropyl) disulfide except that 2-methyl-2-propanethiol replaced 2-butanethiol. After 3 h at 50 °C, the yield (GC) of bis(2-methylpropyl) disulfide and bis(2-methylpropyl) trisulfide were 2.5 and 95.6%, respectively. After 6 h at 50 °C, the yields of disulfide and trisulfide were 3.2 and 95.4%, respectively. Products were identified by comparison with authentic materials.

Dioctyl Disulfide

To a 250 mL, 3-necked flask equipped with a thermowell, magnetic stirring bar, and condenser with a N_2 inlet on top was added 0.30 g of 50% aqueous NaOH solution, 1.93 g of Tergitol® 15-S-7 (Union Carbide), and 60.0 g (0.410 mol) of 1-octanethiol (100% excess). The mixture was heated to 50 °C with stirring. Then 3.3 g (0.103 g-atom) of sulfur (powdered, flowers of sulfur) was added in portions over 5 min. CAUTION: Toxic hydrogen sulfide gas is evolved as a byproduct, and thus this reaction should be carried out in a hood. After all the sulfur was added, the reaction mixture was maintained at 50 °C, and small samples were taken at various times for GC analysis of the disulfide/trisulfide ratio. GC analysis of the final reaction mixture (62.1 g) after 1 h showed that it contained 48.1% dioctyl disulfide along with excess 1-octanethiol. The yield (GC) of dioctyl disulfide was 99.8%. All products were identified by comparison with authentic materials.

Dioctyl disulfide was isolated by adding the reaction mixture to a short column of 70 g of silica gel and eluting with hexane. After removal of the Tergitol and NaOH in this way, excess 1-octanethiol was removed by washing the hexane solution with aqueous 10% NaOH solution (3 times). After drying the hexane solution with anhydrous sodium sulfate and evaporation under reduced pressure, 29.3 g (98% yield) of dioctyl disulfide was obtained.

In a run with triethylamine as catalyst, the procedure and amounts or reagents were the same except that the NaOH and Tergitol were replaced with 0.36 g of triethylamine.

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