

ORGANIC CHEMICALS

Product Information

Mercaptans and Derivative Chemistry

COMPARISON OF MERCAPTANS AND ALCOHOLS

Mercaptans, or thiols, are often referred to as the sulfur analogs of the alcohols; and, indeed, there are many similarities in physical and chemical properties. There are also some notable differences.

Replacement of the oxygen with the larger sulfur atom results in weaker association by hydrogen-bonding between the molecules.

This weaker intermolecular attraction is reflected in lower boiling points for the corresponding mercaptans, at least up to the six-carbon homologs, after which their boiling points become closely similar, because of the relatively smaller influence of the functional group, as shown in Table 1. The bond strength between the hydrogen and the larger sulfur atom is weaker in the case of mercaptans (RSH) than is the oxygen-hydrogen bond strength in alcohols (ROH).

As a result, mercaptans are more reactive, more highly ionized ($\text{RSH} \rightleftharpoons \text{H}^+\text{RS}^-$) and more acidic than alcohols. Mercaptans can be separated from alcohols by caustic extraction. Mercaptans, up to about C_6 , can be readily extracted from hydrocarbons such as naphtha, isooctane, benzene. Above C_6 , however, they become insufficiently soluble in aqueous caustic to permit efficient extractions. This is important to remember when attempting to isolate the higher mercaptans from organic solvents in the laboratory.

Like alcohols, the mercaptans react with carboxylic acids to form esters, in this case



called "thioesters", RCSR' . Likewise, they react with aldehydes and ketones to form acetals and ketals, in this case called "mercaptals", $\text{RCH}(\text{SR})_2$, and "mercaptols", $\text{R}_1\text{R}_2\text{C}(\text{SR})_2$. Unlike the alcohols, which upon oxidation yield aldehydes or ketones, the mercaptans are instead extremely easily oxidized to disulfides, RSSR , and under more vigorous conditions,



to thiosulfates, RSSR , thiosulfonates, RSSR , and finally, in the



presence of water, to sulfinic, RS-OH , and sulfonic, RS-OH , acids.

Methansulfonic acid, also available from ATOFINA, has been shown to be almost as strong an acid as sulfuric acid.

The water solubilities of mercaptans are considerably lower than for the corresponding alcohols (see Table 2). Mercaptans form azeotropes with many hydrocarbons and the mercaptans above methyl and ethyl form azeotropes with their corresponding alcohols.

TABLE I
BOILING POINTS OF MERCAPTANS AND ALCOHOLS °C

	Mercaptan	Alcohol
Methyl	5.96	64.5
Ethyl	34.7	78.3
n-Propyl	67.5	97.2
iso-Propyl	52.9	82.3
n-Butyl	98.0	117.7
n-Pentyl	126.5	137.9
n-Hexyl	151.5	156.5
n-Octyl	199.1	194.7

TABLE II
WATER SOLUBILITIES OF MERCAPTANS & ALCOHOLS

	(grams/liter at 20°C)	
	Mercaptan	Alcohol
Methyl	23.30	∞
Ethyl	6.76	∞
n-Propyl	1.96	∞
n-Butyl	0.57	9.0 ^(a)
n-Hexyl	0.047	--
n-Octyl	0.004	0.054

(a) 15°C

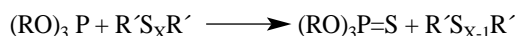
POLYSULFIDES

Mercaptans can be reacted with elemental sulfur at moderate temperatures (50-120°C) in the presence of alkaline catalysts, such as trialkylamines to produce polysulfides. The first step in the reaction sequence is always disulfide formation (with liberation of H₂S). The subsequent insertion of additional sulfur atoms occurs readily. The number of sulfur atoms inserted will depend on the molar ratio of sulfur to mercaptan employed, according to the stoichiometry of the following equations:



Polysulfides above S₅ are generally unstable. The disulfides and trisulfides can be produced in fairly pure form by using appropriate reaction conditions and slightly less than the stoichiometric amounts of sulfur, but the higher S₄ and S₅ polysulfides are generally produced as mixtures containing the tri-, tetra-, and pentasulfides. The higher-dialkyl pentasulfides, such as tert-C₉-S₅-tert-C₉ (TNPS), on standing, tend to precipitate some sulfur and equilibrate at an average sulfur "rank" of about 4.7. Dialkyl polysulfides from C₁ to C₁₂ dialkyl and from S₃ to S₅ sulfur-rank have been prepared in our laboratory.

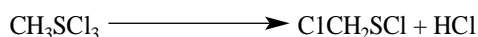
The higher dialkyl polysulfides, such as Elf Atochem's TNPS, find use as extreme-pressure lube additives, especially for cutting oils; the lower dialkyl polysulfides, such as (CH₃)₂S_x, as sulfur-donor agents; for example, to convert phosphites to thiophosphates:



Disulfides and polysulfides are useful for presulfiding hydrotreating catalysts, used in petroleum refining (to convert metal oxides to the preferred metal sulfides).

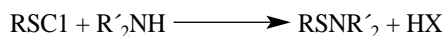
ALKANESULFENYL HALIDES

The sulfenyl halides are prepared by halogenation of mercaptans or disulfides. Sulfenyl iodides, bromides, and chlorides have been prepared either directly from mercaptans $\text{RSH} + \text{X}_2 \longrightarrow \text{RSX} + \text{HX}$, or, often preferably, from the disulfides, $\text{RSSR} + \text{X}_2 \longrightarrow 2\text{RSX}$. Since they are highly reactive, and relatively unstable, preparation is usually at low temperatures in dry, non-polar solvents such as chloroform, carbon tetrachloride, or benzene. Methanesulfenyl chloride can be distilled under vacuum (27-8°C/50-60mmHg), but is unstable on prolonged storage in the presence of light. The tertiary-alkanesulfenyl halide, tert-butylsulfenyl chloride, has considerably better stability. Over-chlorination to produce unstable sulfenyltrichlorides is a problem, the latter decomposing to generate chloroalkanesulfenyl chlorides:



Although the isolation of pure RSCl compounds is often difficult, they are, nevertheless, useful intermediates for the preparation of other, more-stable derivatives.

Reaction of alkanesulfenyl halides with ammonia or amines (low temperature, inert solvent), leads to alkanesulfenamides in high yields:

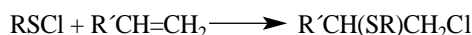


The sulfenamides possess good stability, and, except for some of the lower homologs, are generally recrystallizable solids with sharp melting points.

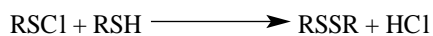
Reaction of RSX with sodium or potassium cyanide, leads to thiocyanates:



Reaction with olefins leads to haloalkyl sulfides:



Sulfenyl halides are intermediates in the oxidation of mercaptans to disulfides with halogens:



SULFIDES, SULFOXIDES, AND SULFONES

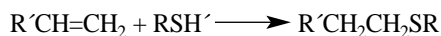
A commonly used method to prepare sulfides is to react a chloride and sodium mercaptide. Mercaptans and alcohols will react in the presence of acidic catalysts, at elevated temperatures (300-400°C), to produce sulfides:



Mercaptans can be added to olefins to produce sulfides. Markovnikov addition occurs readily in the presence of acidic catalysts, at relatively mild temperatures, especially with branched, unsymmetrical (i.e., polarized) olefins.



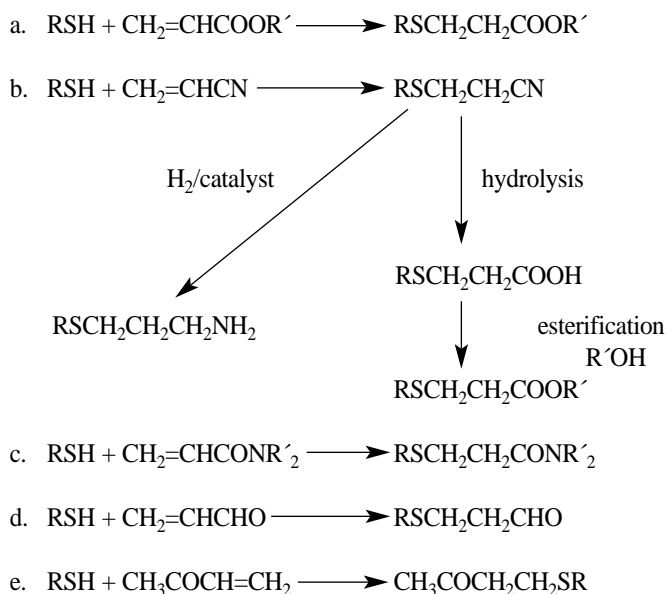
Anti-Markovnikov additions occur in the presence of free-radical catalysts such as peroxides, azo compounds, or ultraviolet light. This reaction proceeds readily, even at room temperature or lower.



So readily does this reaction occur, that care must be taken to avoid using olefins having appreciable peroxide levels when the Markovnikov- addition product is desired, to prevent the isomeric

anti-Markovnikov addition product from being formed as a major byproduct contaminant.

Mercaptans efficiently undergo a Michael type addition in the presence of alkaline catalysts such as triethylamine, to compounds containing an activated double bond, such as acrylate esters, acrylonitrile, acrylamides, acrolein, and vinyl ketones. Lower temperatures (20-100°C) are preferred. The alkylthio group is added to the beta-carbon, as shown below:



Reaction (d), R= methyl, is the first step in the production of the essential amino-acid methionine, $\text{CH}_3\text{SCH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$. The latter is manufactured and used in large quantities as a feed supplement for poultry-feed formulations to improve the weight-gain of the animal per dollar of feed. In the U.S., the equally cost effective "methionine hydroxy analog", $\text{CH}_3\text{SCH}_2\text{CH}_2\text{CH}(\text{OH})\text{COOCa}^{1/2}$ is preferred for this application. The latter is efficiently converted to the active L-methionine by enzymes in the animals' bodies.

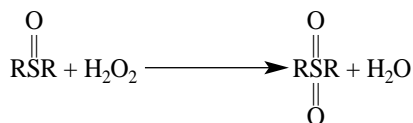
Sulfides are readily oxidized to sulfoxides in the laboratory. Mild temperatures are generally sufficient, and cooling to remove the heat of reaction, rather than heating, is often required. Hydrogen peroxide is the preferred laboratory oxidizing agent, although sodium hypochlorite,



organic peroxides, hydroperoxides, or peracids can also be used. Over-oxidation, producing minor amounts of sulfone as a byproduct, is often a problem, even when no excess of oxidizing agent is used. Lower-dialkyl sulfoxides are stable liquids that can be readily distilled. Commercially, nitrogen oxides, with appropriate catalysts, are used to oxidize dimethyl sulfide to dimethyl sulfoxide (DMSO) continuously in the vapor phase. DMSO is an industrial-used polar solvent.

Further oxidation of sulfoxides leads to sulfones. This reaction is

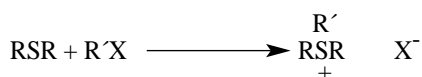
usually carried out in the laboratory with some heating (60-100°C) and cautious initial addition of H_2O_2 . This is to



guard against an excessive buildup of unreacted H_2O_2 due to an induction period, which can then be followed by a sudden exothermic reaction. To avoid this danger, the H_2O_2 reaction can be run with solvent with a catalytic amount of acetic acid present, or in glacial acetic acid as the solvent, to promote smooth reaction via formation of peracetic acid as an intermediate. The use of a minor amount of sodium tungstate as a peroxide-decomposer is also beneficial. The sulfones are generally thermally stable, nicely recrystallizable solids, having sharp melting points.

SULFONIUM SALTS

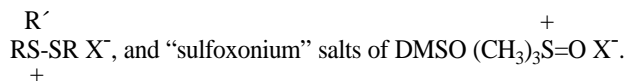
These salts are prepared by reacting alkyl halides with sulfides:



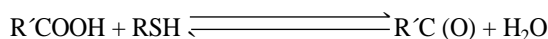
They are generally prepared at room temperature or slightly higher (20-80°C) in organic solvents from which the ionic salt readily precipitates. Alkyl iodides are more reactive than bromides, which are more reactive than chlorides. Nevertheless, the reaction, $\text{CH}_3\text{SCH}_3 + \text{CH}_3\text{Cl} \longrightarrow (\text{CH}_3)_3\text{S}^+\text{Cl}^-$, occurs readily. Steric hindrance is a major factor in sulfonium salt formation; $\text{C}_2\text{H}_5\text{Cl}$, $n\text{-C}_3\text{H}_7\text{Cl}$, $n\text{-C}_4\text{H}_9\text{Cl}$, $\text{tert-C}_4\text{H}_9\text{Cl}$ becoming increasingly much more difficult to react. Likewise, the reaction proceeds much more readily when at least one of the alkyl groups on the sulfide is methyl, or a lower-alkyl.

Although sulfonium-salt formation is more reluctant than comparable quaternary ammonium salt formation, $\text{R}_3\text{N} + \text{R}'\text{X} \longrightarrow \text{R}_3\text{N}^+\text{R}'\text{X}^-$, and the sulfonium salts are thermally less-stable, numerous sulfonium salts have been prepared in high yield and purity. They are true, crystalline salts, all of them being very soluble in water and insoluble in hydrocarbon solvents, even when they contain higher-alkyl groups. They are readily recrystallizable, and generally melt with decomposition at temperatures above 150°C, to form the volatile components, RSR , RSR' , RX , and $\text{R}'\text{X}$.

Little known, but reported in the literature, are the sulfonium salts of dialkyl disulfides,

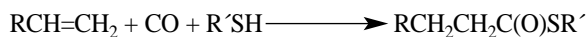


THIOLESTERS



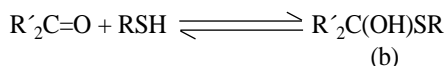
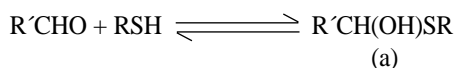
Analogous to the alcohols, an acid-catalyzed equilibrium reaction occurs between mercaptans and carboxylic acids to form thiolesters. The reaction is driven to completion by removal of the byproduct

water. Thioesters can also be prepared by reacting a mercaptan with an acyl chloride, $R'COCl + RSH \longrightarrow R'C(O)SR + HCl$. Recently, technology has been developed to produce thioesters of one-higher carbon content by reacting alpha olefins, carbon monoxide, and a mercaptan at elevated temperature and pressure, in the presence of a palladium catalyst.

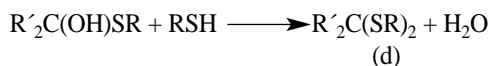
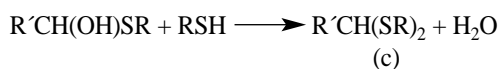


MERCAPTALS AND MERCAPTOLS

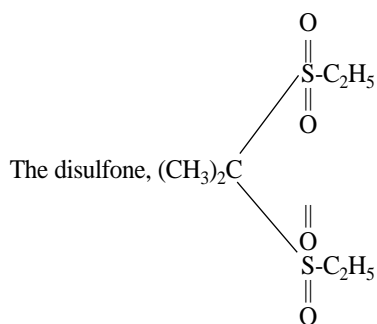
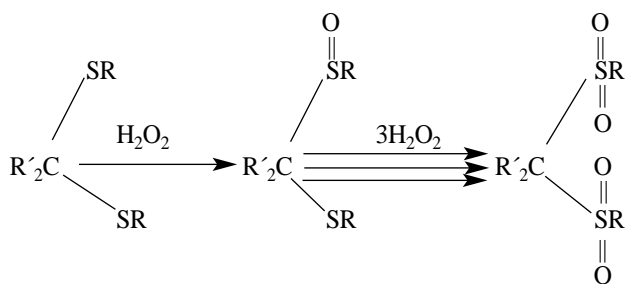
Mercaptals and mercaptols are generally prepared by passing anhydrous HCl into a mixture containing 2 moles of mercaptan per mole of aldehyde (or ketone), without a solvent. The progress of the reaction is measured by the volume of the separated water layer. The first step in this reaction sequence, not requiring acid catalysis, is the equilibrium formation of an unstable hemimercaptal (a) or hemimercaptol (b).



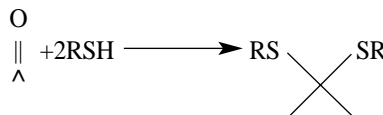
The hemimercaptal or hemimercaptol reacts further, in the presence of the acid catalyst, to form the stable mercaptal (c) or mercaptol (d).



These products can be oxidized stepwise to produce the corresponding sulfoxides and sulfones, as shown below:



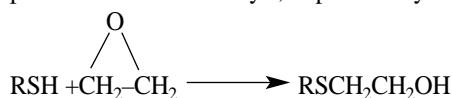
produced from acetone, ethyl mercaptan, and H_2O_2 , is "Sulfonal" which has for many years been known to have medicinal value as a hypnotic. More recently, there is medicinal interest in mercaptol-derivatives of keto-steroids.



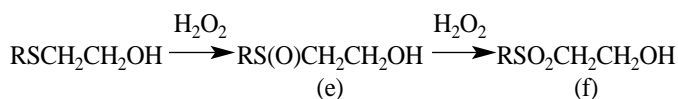
ETHOXYLATED DERIVATIVES

Mercaptans react readily with ethylene oxide and other epoxides such as propylene oxide, epichlorohydrin, cyclohexene oxide, styrene oxide, or glycidol, CH_2-CHCH_2OH , in the

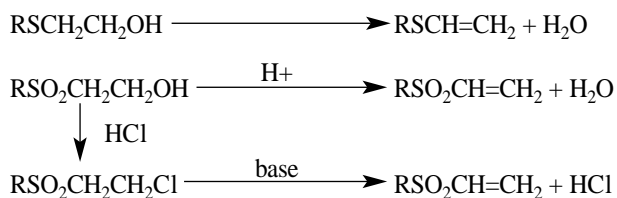
presence of a basic catalyst, to produce hydroxylalkyl sulfides.



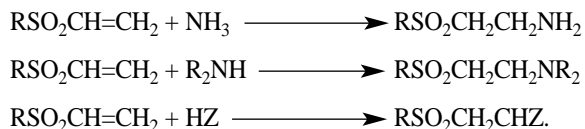
Since the mercapto group in the reactant is more acidic than the alcohol group in the product, the reaction can be terminated at this point, with the addition of one ethylene oxide unit, to give good yields of the 2-alkylthioethanol, in high purity. Oxidation with hydrogen peroxide gives the 2-alkylsulfinyl-(e) and alkylsulfonylethanol (f) in good yields, as shown below:



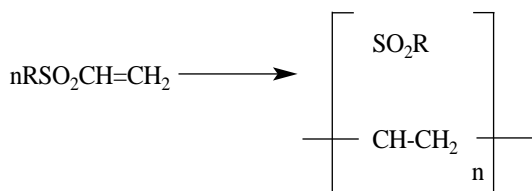
Bubbling anhydrous hydrogen chloride into the 2-alkylthioethanol, without solvent, gives good yields of the half-mustards, $RSCH_2CH_2Cl$. The 2-alkylthioethanol and 2-alkylsulfonylethanol can be dehydrated to produce the alkyl vinyl sulfide and sulfone, respectively. Likewise, the 2-alkylsulfonylethyl chloride is readily dehydrochlorinated in the presence of a base, such as trialkylamine, to produce the alkyl vinyl sulfone. These reactions are shown below:



The double bond of vinyl sulfones is activated by the adjacent polar sulfone group and will undergo facile 1,2-addition reactions with ammonia, amines, and compounds containing an active hydrogen:



In the presence of ultraviolet light and other radiation, vinyl sulfones will homopolymerize.



A weakness of these polysulfones, however, is their sensitivity to alkali, which can attack the acidic hydrogens in the alpha position next to the sulfone group.

With unsymmetrical epoxides, such as propylene oxide or epichlorohydrin, the three-member oxide ring is always cleaved to produce the secondary alcohol in the presence of alkaline catalysts.



The ring opening can be made to go in the opposite direction, to produce the primary alcohols, in the presence of acid catalysts, but this reaction does not proceed as readily.

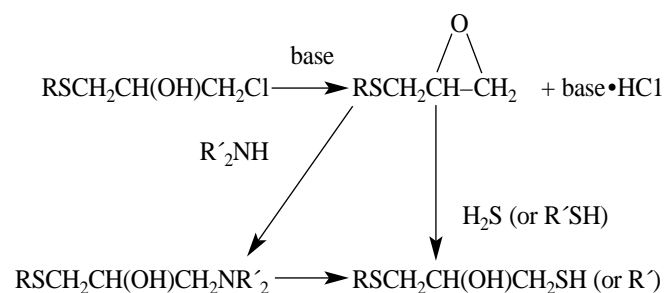


By using higher ethylene oxide to mercaptan ratios, and slightly more vigorous conditions, in the presence of alkali catalyst, the mercaptan can be readily polyethoxylated.



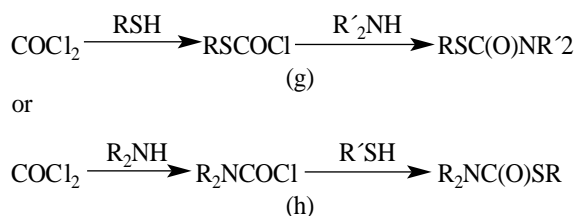
Since the alcohol groups of $\text{RSCH}_2\text{CH}_2\text{OH}$ and $\text{RS}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$ are equally acidic, the polyethoxylated products are generally obtained as mixtures of products containing a range of ethoxy groups, e.g., $\text{RS}(\text{CH}_2\text{CH}_2\text{O})_{1-3}\text{H}$ or $\text{RS}(\text{CH}_2\text{CH}_2\text{O})_{18-22}\text{H}$, depending on the ratio of RSH to $\text{C}_2\text{H}_4\text{O}$ employed. These products, where R is higher alkyl, such as C_8-C_{12} , are useful as non-ionic detergents.

The products from mercaptans and epichlorohydrin can be reacted further to produce trifunctional compounds containing sulfide-alcohol-amine or sulfide-alcohol-mercaptan substituents:

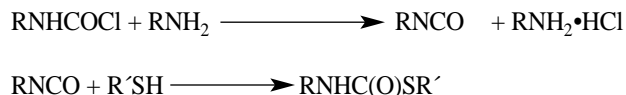


THIOLCARBAMATES

Thiolcarbamate formation is one of the most important reactions of mercaptan chemistry, commercially, since a number of large-volume herbicides and insecticides on the market today are thiolcarbamates. They are the reaction products of one mole of phosgene with one mole of mercaptan and one mole of amine. The reaction sequence can be carried out either way:



Numerous industrial patents exist for both routes. In the one case a chlorothioformate (g) is the intermediate; in the other case, the carbamyl chloride (h) is the intermediate. In the presence of excess primary amine, the carbamyl chloride intermediate, RNHCOCl , is converted to the alkyl isocyanate. The latter reacts readily with mercaptans to produce thiolcarbamates, as shown below:



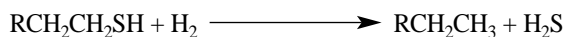
For the reaction of mercaptans with phosgene to form chlorothioformates (g), recent patents claim catalysts such as anionic exchange resins, secondary-amine salts, quaternary ammonium salts, and substituted ureas and thioureas to be effective. For the reaction of mercaptans with carbamyl chlorides (h), a recent patent claims the metals zinc, tin, iron, or "Devarda metal" alloy to be catalytic.

DECOMPOSITION, HYDRODESULFURIZATION

The thermal decomposition of mercaptans generally results in the splitting out of hydrogen sulfide (H_2S) and the formation of an olefin. The H_2S is copiously evolved, but, at the high temperatures generally required for straight thermal decomposition to occur, the olefins may be at least partially polymerized to oils and tars. As with the alcohols, the ease of decomposition is $\text{tert-RSH} > \text{sec-RSH} > \text{primary-RSH}$. In the absence of catalysts or impurities, however, even the tert-mercaptans are generally quite stable and they can be distilled at elevated temperatures up to about 250°C . Ethyl mercaptan is stable to about $380\text{--}400^\circ\text{C}$. In the presence of acidic or basic catalysts, however, these decompositions occur much more readily, at much lower temperatures. In the preparation of mercaptans by continuous processes, for example, a carry-over of catalyst-fines from the reaction zone into the distillation towers can result in serious decomposition, with the generation of H_2S , at relatively low temperatures, such as about 150°C . Sulfides will likewise decompose thermally, and more efficiently in the presence of acidic or basic catalysts, to produce olefins and H_2S .

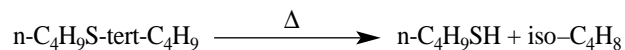
The decompositions of mercaptans and sulfides, with the generation of H_2S , are utilized in the petroleum refining industry for pre-sulfiding hydro-treating catalysts. Hydro-treating, or hydrodesulfurization (HDS), catalysts are generally manufactured as cobalt and molybdenum (and sometimes nickel) oxides on an inert support such as alumina. Prior to use, the metal oxides must be converted to their sulfides. This is generally done by passing a mercaptan or sulfide over the catalyst at elevated temperatures, sufficient to cause decomposition with the generation of H_2S . The H_2S reacts with metal oxides to convert them to the desired metal sulfides. Complete sulfiding of the metal oxides to sulfides is indicated when H_2S -breakthrough is observed in the exit stream from the reactor. Each time the HDS catalysts are air-regenerated to burn off accumulated coke and restore their activity, pre-sulfiding must be repeated to convert the metal oxides back to the sulfide form.

In the HDS process itself, the mercaptans, sulfides, thiophenes, and other organosulfurs, as well as the amines and aromatic nitrogen compounds present in the petroleum fractions, are removed by decomposing them to H_2S and ammonia. In this case, however, olefin fragments, in the presence of hydrogen and catalyst, are converted to alkanes instead of alkenes.

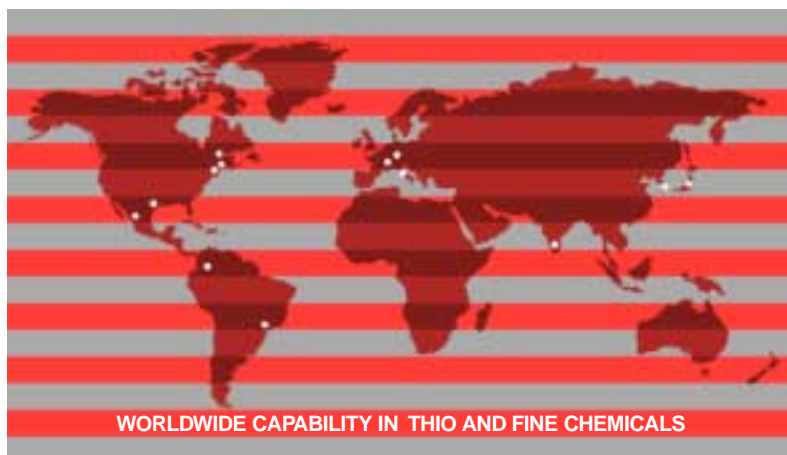


Another industrial application of the decomposition of mercaptans and sulfides to generate H_2S *in situ* is to passivate carbon steel reactor walls, as required, for example, in the commercial thermal dehydrogenation of ethane to produce ethylene.

The initial products from the decomposition of a sulfide are a mercaptan and an olefin. The greater ease of cleavage of the tertiary-carbon-to-sulfur bond, compared with the primary-carbon-to-sulfur bond, can be utilized to prepare mercaptans, as illustrated below:



Acid catalysts are preferred.



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