MERCAPTANS

1. Molecular Structure

2. Chemical Abstracts Service (CAS) Number

3. Registry of Toxic Effects of Chemical Substances (RTECS) Number

The above information for the commercially significant mercaptans (alkyl thiols) is presented in Table 1. Their standard (IUPAC) chemical names are also shown.

In choosing the compounds listed, consideration was given to the amount of production and use in industrial processes.

4. Production Figures and Economic Trends

5. Uses

6. Producer and User Data

Methyl Mercaptan

Based on a production of 17 million lbs. of methionine in 1975 (Althouse, 1976), the 1975 production of methyl mercaptan was about 6 million lbs. Proposed increases in the methionine capacities could more than double the requirement in production of methyl mercaptan (Althouse, 1976).

This compound is used as an intermediate in the production of methionine and as a food supplement in animal feeds (Althouse, 1976; Turk, 1969). Minor uses include applications as a catalyst, jet fuel additive, and in pharmaceuticals (Lawler, 1977).

Producers are as follows (SRI, 1977):

Dow Chem.	Pittsburg, Calif.
Pennwalt Corp.	Beaumont, Tex.
	Greens Bayou, Tex.
Amoco Corp.	Texas City, Tex.

At least two methionine producers and several unknown others use methyl mercaptan.

Ethyl Mercaptan

Based on 1971 production estimates for pesticides synthesized from ethyl mercaptan (Johnson, 1972), approximately 2 million lbs. were produced in 1971.

No growth figures are available.

Table 1. Compounds in the Mercaptan Class

Compound	CAS No.	RTECS No.	Molecular Structure	Standard Chemical Name
Methyl mercaptan	74-93-1	PB43750	CH_3-SH	Methanethiol
Ethyl mercaptan	75-08-1	KI96250	CH_3-CH_2-SH	Ethanethiol
n-Propyl mercaptan	107-03-9	TZ73000	$CH_3-CH_2-CH_2-SH$	Propanethiol
n-Butyl mercaptan	109-79-5	---	$CH_3-(CH_2)_2-CH_2-SH$	Butanethiol
t-Butyl mercaptan	75-66-1	---	$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-SH$	1,1-Dimethylethanethiol

Ethyl mercaptan is used in the synthesis of various pesticides, the largest volume pesticide produced being Eptam® (Ayers et al., 1976; Turk, 1969). Other uses include gas odorants and adhesive stabilizers (Lawler, 1977).

The following companies produce ethyl mercaptan (SRI, 1977):

Helmerich & Payne	Baytown, Tex.
Pennwalt Corp.	Beaumont, Tex.
	Greens Bayou, Tex.
Phillips Petroleum	Phillips, Tex.

Only one producer of pesticides and an unknown number of other companies use ethyl mercaptan.

n-Propyl Mercaptan

Based upon 1971 production estimates for pesticides synthesized from propyl mercaptan (Johnson, 1972), about one million lbs. were produced in 1971.

No growth figures are available.

The primary use of n-propyl mercaptan is as an intermediate in the synthesis of pesticides, particularly Vernam® (Ayers et al., 1976). It is also used as a gas odorant (Lawler, 1977) and polymerization regulator (USITC, 1975).

The Pennwalt Corp. (Greens Bayou, Tex.) and Phillips Petroleum (Phillips, Tex.) produce n-propyl mercaptan (SRI, 1977).

It is used by one major pesticide producer and probably an unknown number of other companies.

n-Butyl Mercaptan

Production figures for n-butyl mercaptan were not encountered.

The major use of n-butyl mercaptan is in the production of organophosphorus compounds and thiolcarbamates; more specifically, insecticides, herbicides, acaricides, and defoliants (Turk, 1969).

The Pennwalt Corp. (Greens Bayou, Tex.) and Phillips Petroleum (Phillips, Tex.) produce n-butyl mercaptan (SRI, 1977).

t-Butyl Mercaptan

Figures for the production of t-butyl mercaptan are not available.

The primary use of t-butyl mercaptan is that of an odorant in the gas industries, serving as a "warning agent" (Turk, 1969).

The following companies produce t-butyl mercaptan (SRI, 1977):

Helmerich and Payne, Inc.	Baytown, Tex.
Pennwalt Corp.	Greens Bayou, Tex.
Phillips Petroleum	Phillips, Tex.

7. Biological Effects of Exposure

Very little information has been encountered on the biological effects of mercaptans. Fairchild and Stokinger (1958) have studied the acute toxicity of ethyl mercaptan, n-propyl mercaptan, n-butyl mercaptan, t-butyl mercaptan, and various other mercaptans of little commercial significance. Little additional information has been obtained from the other sources cited below.

a. Target Organs

All of the commercially significant mercaptans studied by Fairchild and Stokinger (1958) caused similar patterns of organ damage. Single oral or intraperitoneal near-lethal doses of these compounds caused both kidney and liver damage in rats. Kidney damage was usually restricted to cloudy swelling of the tubules and hyaline casts in the lumina. Less commonly, degeneration and necrosis of the tubular epithelium, thickening of Bowman's capsule, and hyaline deposition in glomerular tufts were also noted. Liver damage consisted of lymphocytic infiltration, occasional necrotic foci with small hemmorhages, and varying degrees of fatty swelling or degeneration. In addition to signs of liver and kidney damage, acute inhalation exposures of rats and mice to these mercaptans caused lung damage and irritation of the respiratory tract. Signs of respiratory tract irritation occurred within 15 minutes during inhalation exposures and were evidenced by animals rubbing and closing their eyes, watering of the eyes, and occasional sneezing. Repiratory tract pathology varied from mild to severe hyperemia of the trachea and lungs, capillary engorgement, patchy edema, and occasional hemorrhage (Fairchild and Stokinger, 1958). Acute non-lethal inhalation exposures to methyl mercaptan also is reported to cause lung edema (ACGIH, 1971a). Acute inhalation exposures to n-propyl mercaptan and n-butyl mercaptan also caused corneal opacities in mice. Direct application of 0.1 ml n-propyl mercaptan to the eyes of rabbits caused severe irritation which persisted for up to eight days. This irritation was characterized by a heavy discharge from the eyes, severe redness of the palpebral conjunctivae, and chemosis. The other mercaptans (ethyl, n-butyl, and t-butyl) caused only slight to moderate eye irritation which did not persist past 48 hours (Fairchild and Stokinger, 1958).

b. Acute Effects

Information on the acute toxicity of commercially significant mercaptans is summarized in Table 2. These compounds produced signs of intoxication similar to those caused by hydrogen sulfide (ACGIH, 1971a and b; Fairchild and Stokinger, 1958). Acutely toxic doses of these compounds, given orally or intraperitoneally to rats, or by inhalation to rats and mice, initially caused restlessness, increased respiration, incoordination, and muscular weakness. This was followed by skeletal muscle paralysis, cyanosis, lethargy and/or sedation, respiratory depression, coma, and death. In addition, large oral doses of these mercaptans caused diarrhea in rats (Fairchild and Stokinger,

Table 2. The Acute Toxicity of Some Commercially Significant Mercaptans

Compound	Organism	Route	LD_{50} or LC_{50}	Reference
Methyl mercaptan	Mouse	Subcutaneous	2.4 mg/kg	NIOSH, 1976
Ethyl mercaptan	Rat	Oral	682 mg/kg	Fairchild and Stokinger, 1958
		Intraperitoneal	450 mg/kg	Fairchild and Stokinger, 1958
		Inhalation	4420 ppm x 4 hours	Fairchild and Stokinger, 1958
	Mouse	Inhalation	2770 ppm x 4 hours	Fairchild and Stokinger, 1958
n-Propyl mercaptan	Rat	Oral	1790 mg/kg	Fairchild and Stokinger, 1958
		Intraperitoneal	515 mg/kg	Fairchild and Stokinger, 1958
		Inhalation	7300 ppm x 4 hours	Fairchild and Stokinger, 1958
	Mouse	Inhalation	4010 ppm x 4 hours	Fairchild and Stokinger, 1958
n-Butyl mercaptan	Rat	Oral	1500 mg/kg	Fairchild and Stokinger, 1958
		Intraperitoneal	399 mg/kg	Fairchild and Stokinger, 1958
		Inhalation	4020 ppm x 4 hours	Fairchild and Stokinger, 1958
	Mouse	Inhalation	2500 ppm x 4 hours	Fairchild and Stokinger, 1958
	Dog	Inhalation	700 ppm x 0.5 hours (LC_{LO})	NIOSH, 1976
t-Butyl mercaptan	Rat	Oral	4729 mg/kg	Fairchild and Stokinger, 1958
		Intraperitoneal	590 mg/kg	Fairchild and Stokinger, 1958
		Inhalation	22,200 ppm x 4 hours	Fairchild and Stokinger, 1958
	Mice	Inhalation	16,500 ppm x 4 hours	Fairchild and Stokinger, 1958

1958). Death, in cases of fatal exposure to methyl mercaptan, has been attributed to respiratory paralysis (ACGIH, 1971a). Fairchild and Stokinger (1958) have noted that even-numbered carbon straight chain mercaptans are significantly more toxic by all routes of administration than are n-propyl or t-butyl mercaptan and that mice are more susceptible than rats to inhalation exposures.

c. Subchronic Effects

No information has been encountered.

d. Chronic Effects

A summary of a Russian study (Blinova, 1965) indicates that the chronic inhalation "threshold effect" for ethyl mercaptan exposure to small animals is 40 ppm. Neither species nor duration of exposure are specified (ACGIH, 1971c).

e. Human Effects

Ethyl mercaptan, at concentrations of about 4 ppm, caused headache nausea, and irritation in exposed humans. Concentrations of about 0.4 ppm caused no detectable effects (ACGIH, 1971b). At unspecified high concentrations, this mercaptan is reported to cause collapse, cyanosis, increased pulse rate, and convulsions (Moeschlin, 1965).

A case of accidental inhalation exposure to methyl mercaptan reportedly led to coma, the development of acute hemolytic anemia, methemoglobinemia, and death (ACGIH, 1971a).

8. TLV

The time-weighted average limits for methyl mercaptan, ethyl mercaptan, and n-butyl mercaptan are all set at 0.5 ppm (ACGIH, 1971a, 1971b, and 1971c).

9. Other Standards

OSHA (1974) has set ceiling limits for exposure to methyl mercaptan, ethyl mercaptan, and n-butyl mercaptan at 10 ppm.

10. Other Data

The odor threshold for n-butyl mercaptan is 0.01 to 0.0001 ppm (ACGIH, 1971c). Similarly, the unpleasant odor of both methyl mercaptan and ethyl mercaptan make it unlikely that the TLV's for these compounds could be inadvertently exceeded in the workplace (ACGIH, 1971a and 1971b).

While the toxicologic properties of the commercially significant mercaptans discussed in previous sections are relatively similar to each other, certain other mercaptans may act quite differently. Fairchild and Stokinger (1958) found that t-octyl mercaptan, unlike these other mercaptans, caused central

nervous system stimulation. This observation may be significant in considering the potential hazards of commercially significant higher molecular weight mercaptans (e.g., n-octyl mercaptan) on which no toxicity information was encountered.

Table 3 lists the number of reported human exposures to various mercaptans (NIOSH, 1977).

Table 3. Reported Human Occupational Exposures To Mercaptans (NIOSH, 1977)

Compound	Number of Exposures
Methyl mercaptan	19,140
Ethyl mercaptan	23,130
n-,sec-,t-Butyl mercaptans	19,410
n-Octyl mercaptans	18,660
t-,n-Dodecyl mercaptans	21,150

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