

TETRANITROMETHANE

1. Exposure Data

1.1 Chemical and physical data

1.1.1 Nomenclature

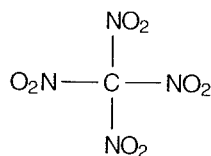
Chem. Abstr. Serv. Reg. No.: 509-14-8

Chem. Abstr. Name: Tetranitromethane

IUPAC Systematic Name: Tetranitromethane

Synonyms: Tetan; TNM

1.1.2 Structural and molecular formulae and relative molecular mass



CN_4O_8

Relative molecular mass: 196.04

1.1.3 Chemical and physical properties of the pure substance

- (a) *Description:* Pale yellow liquid with a pungent odour (Budavari, 1989; Lewis, 1993)
- (b) *Boiling-point:* 126 °C (Lide, 1993)
- (c) *Melting-point:* 14.2 °C (Lide, 1993)
- (d) *Density:* 1.6380 at 20 °C/4 °C (Lide, 1993)
- (e) *Spectroscopy data:* Infrared (prism [2492], grating [29557]) and mass spectral data have been reported (Sadtlter Research Laboratories, 1980)
- (f) *Solubility:* Insoluble in water; soluble in alcoholic potassium hydroxide, diethyl ether and ethanol (Budavari, 1989; Davis, 1993; Lide, 1993)
- (g) *Volatility:* Vapour pressure, 8.4 mm Hg [1.1 kPa] at 20 °C; relative vapour density (air = 1), 0.8 (Davis, 1993)
- (h) *Stability:* Highly explosive when exposed to heat or shock; mixtures with amines (e.g. aniline) ignite spontaneously and may explode. Mixtures with cotton or toluene may explode when ignited. Forms sensitive and powerful explosive mixtures with nitrobenzene, 1-nitrotoluene, 4-nitrotoluene, 1,3-dinitrobenzene,

1-nitronaphthalene, other oxygen-deficient explosives and hydrocarbons (Sax & Lewis, 1989)

(i) *Octanol/water partition coefficient (P)*: $\log P, -0.791$ (United States National Library of Medicine, 1995)

(j) *Conversion factor*: $\text{mg/m}^3 = 8.02 \times \text{ppm}^1$

1.1.4 *Technical products and impurities*

Tetranitromethane is available commercially at an unknown purity (Aldrich Chemical Co., 1994).

1.1.5 *Analysis*

Early methods (1940–59) of determining nitroalkanes used colorimetric procedures. Since 1970, these have been replaced by instrumental methods, primarily gas chromatography, mass spectrometry and infrared spectroscopy (Davis, 1993).

Tetranitromethane can be determined in air using gas chromatography with alkali-flame ionization detection (Taylor, 1977).

1.2 **Production and use**

1.2.1 *Production*

Tetranitromethane can be prepared by nitration of acetic anhydride with anhydrous nitric acid (Budavari, 1989) or by reacting fuming nitric acid with benzene or acetylene (Lewis, 1993). It has also been prepared by nitration of acetylene with excess nitric acid to form a mixture of trinitromethane and nitric acid, which can be converted to tetranitromethane by sulfuric acid at elevated temperatures (Stockinger, 1982).

Tetranitromethane is produced by one company in the United States of America and one company in Russia (Chemical Information Services, 1994).

1.2.2 *Use*

Tetranitromethane has been used as an oxidizer in rocket propellants, as an explosive in admixture with toluene (see IARC, 1989a) and to increase the cetane number of diesel fuels (see IARC, 1989b); it has also been used as a reagent for detecting the presence of double bonds in organic compounds and for nitration of tyrosine in proteins and peptides (Budavari, 1989; American Conference of Governmental Industrial Hygienists, 1991; Lewis, 1993).

¹Calculated from: $\text{mg/m}^3 = (\text{relative molecular mass}/24.45) \times \text{ppm}$, assuming temperature (25 °C) and pressure (101 kPa)

1.3 Occurrence

1.3.1 *Natural occurrence*

Tetranitromethane is not known to occur as a natural product.

1.3.2 *Occupational exposure*

The National Occupational Exposure Survey conducted between 1981 and 1983 indicated that 4350 employees in the United States were potentially exposed to tetranitromethane. The estimate is based on a survey of companies and did not involve measurements of actual exposure (United States National Institute for Occupational Safety and Health, 1995).

1.3.3 *Environmental occurrence*

No information was available to the Working Group.

1.4 Regulations and guidelines

Occupational exposure limits and guidelines for tetranitromethane in several countries are presented in Table 1.

Table 1. Occupational exposure limits and guidelines for tetranitromethane

Country	Year	Concentration (mg/m ³)	Interpretation
Argentina	1991	8	TWA
Australia	1993	8	TWA
Belgium	1993	8	TWA
Bulgaria ^a	1995	0.04	TWA
Canada	1991	8	TWA
Colombia ^a	1995	0.04	TWA
Denmark	1993	8	TWA
Finland	1993	8	TWA
		24	STEL
France	1993	8	TWA
Germany	1995	None, IIIA2 ^b	MAK
Jordan ^a	1995	0.04	TWA
Mexico	1991	8	TWA
Netherlands	1994	8	TWA
New Zealand ^a	1995	0.04	TWA
Philippines	1993	8	TWA
Republic of Korea ^a	1995	0.04	TWA
Russia	1993	0.3	STEL
Singapore ^a	1995	0.04	TWA
Switzerland	1993	8	TWA
Turkey	1993	8	TWA

Table 1 (contd)

Country	Year	Concentration (mg/m ³)	Interpretation
USA			
ACGIH (TLV)	1995	0.04, A2 ^b	TWA
OSHA (PEL)	1994	8	TWA
NIOSH (REL)	1994	8	TWA
Viet Nam ^a	1995	0.04	TWA

From Työministeriö (1993); Arbeitsinspectie (1994); US National Institute for Occupational Safety and Health (NIOSH) (1994a,b); US Occupational Safety and Health Administration (OSHA) (1994); American Conference of Governmental Industrial Hygienists (ACGIH) (1995); Deutsche Forschungsgemeinschaft (1995); United Nations Environment Programme (1995)

TWA, time-weighted average; STEL, short-term exposure limit; MAK, maximum workplace concentration; TLV, threshold limit value; PEL, permissible exposure limit; REL, recommended exposure limit

^aFollows ACGIH values

^bIIIA2, substances shown to be clearly carcinogenic only in animal studies but under conditions indicative of carcinogenic potential at the workplace; A2, suspected human carcinogen

2. Studies of Cancer in Humans

No data were available to the Working Group.

3. Studies of Cancer in Experimental Animals

3.1 Inhalation exposure

3.1.1 *Mouse*

Groups of 50 male and 50 female B6C3F1 mice, eight to 10 weeks of age, were exposed to air containing target concentrations of 0, 0.5 or 2 ppm [0, 4 or 16 mg/m³] tetranitromethane (approximately 100% pure) for 6 h per day on five days per week for 103 weeks. Additional groups of six male mice were exposed to 0 or 2 ppm and 10 male mice were exposed to 0.5 ppm for 52 weeks. All animals received complete histopathological evaluation. Monitoring indicated that the mean daily chamber concentrations were within $\pm 10\%$ of the target concentrations on more than 96% of the study days. In the 52-week study, multiple alveolar-bronchiolar adenomas were found in the lung of one mouse in the 2-ppm group. Hepatocellular adenomas were found in the livers of four

mice in the 0.5-ppm group. In the 103-week study, body weights of exposed mice were generally 5–10% lower than those of controls. Survival at 103 weeks was decreased in exposed males (37/50 in controls, 26/50 at the low dose, 15/50 at the high dose) but was unchanged in females (31/50 in controls, 28/50 at the low dose, 24/50 at the high dose). The incidences of alveolar–bronchiolar neoplasms were increased in exposed males and females; those of both adenomas and carcinomas were markedly increased over controls (alveolar–bronchiolar adenomas and carcinomas: males — 12/50 in controls, 27/50 at the low dose, 47/50 at the high dose; females — 4/49 in controls, 24/50 at the low dose, 49/50 at the high dose; $p < 0.001$, logistic regression trend analysis). The incidences of hyperplasia of the alveolar epithelium and of the bronchioles were significantly increased in all treated males and females. No increase in the incidence of hepatocellular adenomas was seen in the 103-week study (United States National Toxicology Program, 1990; Bucher *et al.*, 1991).

3.1.2 Rat

Groups of 50 male and 50 female Fischer 344/N rats, six to seven weeks of age, were exposed to air containing target concentrations of 0, 2 or 5 ppm [0, 16 or 40 mg/m³] tetra-nitromethane (approximately 100% pure) for 6 h per day on five days per week for 103 weeks. Monitoring indicated that the mean daily chamber concentrations were within $\pm 10\%$ of the target concentrations on more than 99% of the study days. All animals received complete histopathological examination. Body weights of exposed rats were generally 5–10% lower than those of controls. Survival at 103 weeks was decreased in high-dose males (18/50 in controls, 17/50 at the low dose, 4/50 at the high dose) but was unchanged in females (25/50 in controls, 34/50 at the low dose, 15/50 at the high dose). The incidences of alveolar–bronchiolar neoplasms were increased in treated males and females; those of both adenomas and carcinomas were markedly increased over controls (alveolar–bronchiolar adenomas and carcinomas: males — 1/50 in controls, 33/50 at the low dose, 46/50 at the high dose; females — 0/50 in controls, 22/50 at the low dose, 50/50 at the high dose; $p < 0.001$, logistic regression analysis). The incidence of squamous-cell carcinomas of the lung was also significantly increased in high-dose males and females (males — 0/50 in controls, 1/50 at the low dose, 19/50 at the high dose; females — 0/50 in controls, 1/50 at the low dose, 12/50 at the high dose; $p < 0.001$, life-table analysis). The incidences of hyperplasia of the alveolar epithelium and of the bronchioles were significantly increased in all treated males and females (United States National Toxicology Program, 1990; Bucher *et al.*, 1991).

4. Other Data Relevant for an Evaluation of Carcinogenicity and its Mechanisms

4.1 Absorption, distribution, metabolism and excretion

4.1.1 Humans

No data were available to the Working Group.

4.1.2 *Experimental systems*

No studies have been published on the pharmacokinetics and metabolism of tetranitromethane in laboratory animals.

4.2 Toxic effects

4.2.1 *Humans*

No data were available to the Working Group.

4.2.2 *Experimental systems*

(a) *Single-dose studies*

In experiments of inhalation exposure of rats [strain unspecified] at different concentrations of tetranitromethane, the times to 50% lethality were reported to be 36 min at 1230 ppm [9840 mg/m³], 60 min at 300 ppm [2400 mg/m³] and 5.8 h at 33 ppm [264 mg/m³] (Horn, 1954).

(b) *Repeated-dose studies*

Male and female Fischer 344/N rats were exposed by inhalation to 2, 5, 10 or 25 ppm [16, 40, 80 or 200 mg/m³] tetranitromethane for 6 h per day on five days per week for 14 days (United States National Toxicology Program, 1990). All exposed rats were lethargic. All rats exposed to 25 ppm tetranitromethane died on the first day and two had pulmonary oedema. At 10 ppm, body-weight depression was observed in males and females.

Male and female B6C3F1 mice were exposed by inhalation to 2, 5, 10, 25 or 50 ppm [16, 40, 80, 200 or 400 mg/m³] tetranitromethane for 6 h per day on five days per week for 14 days (United States National Toxicology Program, 1990). All mice exposed to 50 ppm died on day two. Three of five males and all females exposed to 25 ppm died before the end of the study. Body-weight depression was observed in males exposed to 5 ppm or above and in females exposed to 10 ppm. Mice that survived exposures of 10 or 25 ppm were observed to have inflamed, reddened lungs.

Male and female B6C3F1 mice and Fischer 344/N rats were exposed by inhalation to 0.2, 0.7, 2, 5 and 10 ppm [0.8, 5.6, 16, 40 and 80 mg/m³] tetranitromethane for 13 weeks. Mean body-weight depression, lethargy and serous exudate in the nasal passage were observed in male and female rats and mice exposed to 10 ppm. In addition, chronic lung inflammation was present in rats. No compound-related death occurred. Focal squamous metaplasia of the respiratory epithelium of the nasal mucosa was observed in 40% of the female rats exposed to 10 ppm, but not in those exposed to 5 ppm. Focal squamous metaplasia (mild) of the respiratory epithelium of the nasal mucosa was also observed in mice. Dyspnoea (at 10 ppm) and inflammation of the nasal mucosa (at 5 and 10 ppm) were observed in mice. Increases in relative liver weight were seen at all dose levels in male and female rats and male mice (United States National Toxicology Program, 1990).

Male and female F344/N rats and B6C3F1 mice were exposed by inhalation to 2 or 5 ppm and 0.5 or 2 ppm tetranitromethane, respectively, for two years (United States

National Toxicology Program, 1990). The incidence of inflammation of the nasal mucosa in rats was increased, relative to controls, at 5 ppm. In mice, significant increases in nasal lumen exudate were associated with exposure of males and females to 2 ppm and 0.5 ppm, respectively.

(c) *In-vitro systems*

The ability of tetranitromethane to nitrate tyrosine residues in proteins selectively has been used to investigate enzyme and receptor-active sites. Incubation of horse erythrocyte glutathione transferase resulted in a complete loss of enzyme activity (Del Boccio *et al.*, 1991). Approximately 25 μM cytochrome P450 LM4 (CYP1A2; prepared from liver microsomes of phenobarbital-pretreated rabbits) was incubated with 50 μM tetranitromethane at 25 °C, pH 7.5 (Jänig *et al.*, 1987). The modified enzyme possessed reduced 4-nitrophenetole *O*-deethylase activity (20% of control), increased binding affinity for 4-nitrophenetole, decreased binding affinity for α -naphthoflavone and metyrapone and a reduced rate of electron transfer from NADPH-cytochrome P450 reductase.

Brain and heart muscarinic receptors have been modified by incubation of tetranitromethane (50 μM) with homogenates (0.5 mg protein/mL) from male CD rats for 20 min at 25 °C and pH 8.1. An increased affinity for the agonist acetylcholine was observed in membranes from the striatum, hippocampus, cerebral cortex and heart atrium, but not the brain stem (Gurwitz & Sokolovsky, 1985a,b). Similar results were obtained by incubating cortical slices with 300 μM tetranitromethane (Gurwitz & Sokolovsky, 1985b). Incubation of bovine adrenal medullary microsomes with tetranitromethane (10–100 μM for 20 min at 25 °C and pH 8) caused a concentration-dependent, irreversible decrease in the number of muscarinic binding sites and binding affinity (Yamanaka *et al.*, 1988).

4.3 Reproductive and developmental effects

No data were available to the Working Group.

4.4 Genetic and related effects

4.4.1 *Humans*

No data were available to the Working Group.

4.4.2 *Experimental systems* (see also Table 2 and Appendices 1 and 2)

(a) *Mutation and allied effects*

Tetranitromethane with and without metabolic activation by S9-mix was mutagenic in *Salmonella typhimurium* TA98, TA100 and TA1535 but negative in TA1537. Tetranitromethane did not induce deletion mutation; it induced chromosomal aberrations and sister chromatid exchange in Chinese hamster ovary cells.

Table 2. Genetic and related effects of tetranitromethane

Test system	Result ^a		Dose ^b (LED/HID)	Reference
	Without exogenous metabolic system	With exogenous metabolic system		
SA0, <i>Salmonella typhimurium</i> TA100, reverse mutation	+	(+)	1.5	Kawai <i>et al.</i> (1987)
SA0, <i>Salmonella typhimurium</i> TA100, reverse mutation	(+)	+	1.25	Zeiger <i>et al.</i> (1987)
SA0, <i>Salmonella typhimurium</i> TA100, reverse mutation	+	+	4.0	Würgler <i>et al.</i> (1990)
SA2, <i>Salmonella typhimurium</i> TA102, reverse mutation	-	+	33	Würgler <i>et al.</i> (1990)
SA5, <i>Salmonella typhimurium</i> TA1535, reverse mutation	+	+	0.75	Zeiger <i>et al.</i> (1987)
SA7, <i>Salmonella typhimurium</i> TA1537, reverse mutation	-	-	38	Zeiger <i>et al.</i> (1987)
SA9, <i>Salmonella typhimurium</i> TA98, reverse mutation	-	-	500	Kawai <i>et al.</i> (1987)
SA9, <i>Salmonella typhimurium</i> TA98, reverse mutation	+	(+)	4.0	Würgler <i>et al.</i> (1990)
SA9, <i>Salmonella typhimurium</i> TA98, reverse mutation	(+)	(+)	1.0	Zeiger <i>et al.</i> (1992)
SAS, <i>Salmonella typhimurium</i> TA97, reverse mutation	+	(+)	8.0	Würgler <i>et al.</i> (1990)
SAS, <i>Salmonella typhimurium</i> LT2, deletion mutation	-	0	4000	Alper & Ames (1975)
ECW, <i>Escherichia coli</i> WP2 <i>uvrA</i> , reverse mutation	+	+	1.0	Kawai <i>et al.</i> (1987)
SIC, Sister chromatid exchange, Chinese hamster ovary CHO cells <i>in vitro</i>	+	-	1.7	US National Toxicology Program (1990)
CIC, Chromosomal aberrations, Chinese hamster ovary CHO cells <i>in vitro</i>	-	(+)	20	US National Toxicology Program (1990)

^a +, positive; (+), weak positive; -, negative; 0, not tested; ?, inconclusive

^b LED, lowest effective dose; HID, highest ineffective dose. In-vitro tests, µg/mL; in-vivo tests, mg/kg bw

(b) *Mutational spectra*

Dominant transforming genes were studied in lung tumours from Fischer 344 rats and C57Bl/6 × C3H F₁ mice exposed chronically by inhalation to tetranitromethane. All of the 10 rat tumours tested and all of the nine mouse tumours tested had a GC → AT transition in the second base of codon 12 of the *K-ras* oncogene (Stowers *et al.*, 1987; You *et al.*, 1991).

5. Summary of Data Reported and Evaluation

5.1 Exposure data

Tetranitromethane is produced commercially by nitration of acetic anhydride or acetylene. Tetranitromethane has been used as an oxidizer in rocket propellants and explosives. Few data are available on human exposure to tetranitromethane.

5.2 Human carcinogenicity data

No data were available to the Working Group.

5.3 Animal carcinogenicity data

Tetranitromethane was tested for carcinogenicity in one study in mice and in one study in rats by inhalation exposure. The incidence of alveolar-bronchiolar adenomas and carcinomas was markedly increased in treated mice and rats, and the incidence of squamous-cell carcinomas of the lung was increased in treated rats.

5.4 Other relevant data

No human or experimental animal data were available to the Working Group on the absorption, distribution, metabolism or excretion of tetranitromethane.

No human data were available on the toxic effects of tetranitromethane.

Tetranitromethane induced lethargy, reduced body-weight gain and inflammatory changes in the upper and lower respiratory tract of rats and mice.

Tetranitromethane is genotoxic in bacteria and cultured mammalian cells. Tumours from tetranitromethane-treated rats and mice had a GC → AT transition in the second base of codon 12 of the *K-ras* oncogene.

5.5 Evaluation¹

There is *inadequate evidence* in humans for the carcinogenicity of tetranitromethane.

¹For definition of the italicized terms, see Preamble, pp. 24–27.

There is *sufficient evidence* in experimental animals for the carcinogenicity of tetranitromethane.

Overall evaluation

Tetranitromethane is *possibly carcinogenic to humans (Group 2B)*.

6. References

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