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FORMALDEHYDE TOXICITY

Smoker 0.4 mg formaldehyde/day (S) Edited by

James E. Gibson

Chemical Industry Institute of Toxicology

* Methanol

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(C)

formaldehyde dehydrogenase
methanol → formic acid
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no formaldehyde

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Overview of Formaldehyde

Gordon W. Newell

It was only a few years ago that the innovative urea-formaldehyde foam process was introduced as a new system for insulating residences. Shortly thereafter, however, complaints about formaldehyde odors in certain residences treated by this process prompted a flurry of investigations into the problem. Subsequent concerns about irritation and headaches in some of the exposed populations were compounded by a report from the Chemical Industry Institute of Toxicology: in a CIIT-sponsored inhalation study, rats developed squamous cell carcinomas in the nasal cavity when exposed for long periods to 15 ppm concentrations of formaldehyde.

In this presentation I will touch briefly on the chemistry, occurrence, biochemistry, environmental/occupational exposure, and health effects of formaldehyde. Much of the information has been taken from two National Academy of Sciences publications: "Formaldehyde—An Assessment of Its Health Effects," published in March (1980) by the Committee on Toxicology, and a report of the Committee on Aldehydes, "Formaldehyde and Other Aldehydes," published in December (1981).

PROPERTIES OF FORMALDEHYDE

Monomeric formaldehyde is a colorless gas that condenses to form a liquid of high vapor pressure that boils at -19°C ; it forms a crystalline solid at -118°C . It has a pungent odor that is highly irritating to the exposed membranes of the eyes, nose, and upper respiratory tract. In the pure, dry, liquid form at low temperatures (-90 to -117°C) it polymerizes slowly; its stability depends on its purity, and it must be held at low temperature to avoid polymerization.

Trioxane is the cyclic trimer of formaldehyde; it has the empirical formula of $\text{C}_3\text{H}_6\text{O}_3$, with three formaldehyde units per molecule. In pure form, it is a colorless, crystalline solid that melts at $61-62^{\circ}\text{C}$ and boils at 115°C . It has a chloroformlike odor but is not irritating. It is soluble in water but is combustible and burns readily when ignited.

Paraformaldehyde contains eight structural units of formaldehyde. It is a colorless solid in a granular form with an odor characteristic of monomeric formaldehyde. Paraformaldehyde melts over a wide temperature range, which depends on the degree of polymerization. At room temperatures, it gradually vaporizes largely as a monomeric formaldehyde with some water formation; the rate is increased by heating. Thus, it is commonly used as a source of formaldehyde for disinfecting large areas.

Formalin is the principal form in which formaldehyde is marketed; it is an aqueous solution that ranges in concentration from 37 to 50 percent by weight. It is a clear solution with a strong, pungent odor of formaldehyde. The solution is slightly acidic.

Formaldehyde vapor is relatively stable with respect to thermal decomposition; at temperatures above 400°C , it decomposes to form carbon monoxide, hydrogen, and methanol. In the aqueous phase, formaldehyde is oxidized readily by even mild oxidizing agents; this property has been exploited in the development of several wet, chemical, analytical methods for formaldehyde.

When oxidized under controlled conditions, in the gaseous or dissolved state, formaldehyde may be converted in part to formic acid or, under more highly oxidative conditions, to carbon monoxide and water. The photo-oxidation of formaldehyde in the gas phase leads to carbon monoxide, hydrogen, hydrogen peroxide, formic acid, and some other meta-stable products.

The formation of resinous products on reaction with other chemicals is one of the most useful characteristics of formaldehyde and is the reason for its immense importance in the synthetic resin industry. Under suitable conditions, the molecules of many compounds are linked together by methylene groups when subjected to the action of formaldehyde. Phenol- and urea-formaldehyde resins are polymethylene compounds of this type. Two distinct mechanisms are probably involved in resin-forming reactions: the polycondensation of simple methyl derivatives and the polymerization of double-bonded methylene compounds.

Thermoplastic resins are the result of simple linear condensations, whereas the production of thermosetting resins involves the formation of methylene cross-linkage between linear chains. Both types may be produced from the same raw materials by variations in the relative amounts of formaldehyde used, the condition of the catalysts, and the temperature. However, with compounds whose molecules present only two reactive hydrogen atoms, only thermoplastic resins can be obtained.

SOURCES AND OCCURRENCES OF FORMALDEHYDE

Formaldehyde emissions from industrial processes are generally confined to the immediate vicinity of the plant. Primary sources of potential public exposure include cigarette smoke, automotive exhaust, photochemical smog, incinerators, and degassing of urea-formaldehyde resinous products (industrial processes).

Incomplete combustion of hydrocarbons accounts for much of the formaldehyde present in the atmosphere. Automotive exhausts have been reported to contain formaldehyde at 29-43 ppm (1). Mobile sources (automobiles, diesel engines, and aircraft engines) emit approximately 666 million pounds of formaldehyde annually. Local concentrations may vary with traffic patterns and vehicular density.

Municipal incinerators emit about 0.6-0.9 pound of formaldehyde per ton of refuse, or 13.1 million pounds of formaldehyde annually (2).

Photochemical smog can be an important source of formaldehyde. Stupfel (3) reported that outdoor air in Los Angeles contained formaldehyde at 0.05-0.12 ppm over the course of 26 days of measurements. A heavy smoker can be exposed to a considerable amount of formaldehyde. Cigarette smoke contains as much as 40 ppm of formaldehyde by volume (4, 5). With 95 percent retention from ten 40-ml puffs on each of 20 cigarettes, a smoker could receive a total daily burden of approximately 0.4 mg of formaldehyde.

Other potential sources of formaldehyde in the home include combustion and gas stoves, heaters, and breakdown of cooking oils. Hallowell et al. (6) measured total aliphatic aldehydes in indoor air. After human occupation of an experimental house, total aldehydes increased threefold to 0.116 ppm. The ventilation rate was only 0.02 air exchanges each hour.

A recent study of 15 occupied residential units revealed formaldehyde concentrations of less than 0.12 ppm in 11 of the units (7). Concentrations as high as 0.38 and 0.31 ppm were found in two of the units, which were mobile homes containing particleboard. Formaldehyde concentrations of 0.03-2.5 ppm were measured in 74 mobile homes whose occupants complained of odor and irritation thought to be associated with the use of particleboard (8). Repeat measurements on two homes indicated half-lives (time for concentrations to decrease by 50 percent) of 45 and 110 days. A Scandinavian study using field tests and mathematical models indicated a half-life of 2 years (9). The rate of